PB-221 494

SECONDARY WASTE TREATMENT FOR A SMALL DIVERSIFIED TANNERY

E. L. Thackston

Caldwell Lace Leather Company

Prepared for:

Environmental Protection Agency

April 1973

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

EPA-R2-73-209
APRIL 1973
W73-11340

Environmental Protection Technology Series

PB 221 494

Secondary Waste Treatment for A Small Diversified Tannery

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

Office of Research and Monitoring
U.S. Environmental Protection Agency
Washington, D.C. 20460

82

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Monitoring, Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

1. Report No. 2. W 73-11340

Secondary Waste Treatment for a Small Diversified Tannery, (all caps)

5. Report Date
6.
8. Performing Organization Report No.

Thackston, E. L.

EPA Project 12120 EFM

Caldwell Lace Leather Company
Auburn, Kentucky

WPRD 25-01

13. Type of Report and Period Covered

12. Sponsoring Organization

Environmental Protection Agency, report number, EPA-R2-73-209, April 1973. (Technology Series) 75p, 13 fig, 24 tab, 30 ref

The Caldwell Lace Leather Co. of Auburn, Kentucky, a small tannery using primarily alum tanning but some chrome and vegetable tanning, received a demonstration grant in 1967 from the FWPCA to investigate and demonstrate methods of treating tannery wastes for discharge to a small stream. A research contract with Vanderbilt University produced findings which have previously been reported and are reviewed herein.

A modified completely-mixed activated sludge plant was constructed, along with facilities to handle specific problem wastes. After (or had been) operating for a year, an EPA survey team conducted a study which showed that the plant was performing as predicted by the research phase, except for solids carryover from the secondary clarifier due to mechanical problems. After the problems were corrected, the plant began producing an effluent which more than met expectations, removing 97% of the suspended solids and 95% of the BOD. Due to conservation measures inside the tannery, however, the load on the plant is somewhat less than the design load, so the plant is operating as an extended aeration plant. (EPA)

17a. Descriptors

*Wastewater treatment, *activated sludge, *industrial wastes, testing, ~~research and development~~, evaluation, laboratory tests, sampling, ~~acceptance testing~~, settling basins, chemical oxygen demand, biochemical oxygen demand, *Kentucky

17b. Identifiers

*Tannery wastes, leather production

73-209

Copy available from GPO Sup Doc as EP1.23/2:, $1.25 ; microfiche from NTIS as PB 221 494, $0.95.

17c. COSATI Field/Group 05 D

19. Security Class. (Report)	21. No. of Pages	Send To:
20. Security Class. (Page)	22. Price	WATER RESOURCES SCIENTIFIC INFORMATION CENTER U S DEPARTMENT OF THE INTERIOR WASHINGTON D C 20240

Edward L. Thackston

EPA-R2-73-209
April 1973

SECONDARY WASTE TREATMENT FOR A SMALL DIVERSIFIED TANNERY

by

Edward L. Thackston

Grant No. WPRD 25-01
Project 12120 EFM

Project Officers

James J. Westrick
James Kreissl
U.S. Environmental Protection Agency
National Environmental Research Center
Cincinnati, Ohio 45268

Prepared for

OFFICE OF RESEARCH AND MONITORING
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402
Price $1.25 domestic postpaid or $1 GPO Bookstore

ib

EPA REVIEW NOTICE

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

The Caldwell Lace Leather Co. of Auburn, Kentucky, a small tannery using primarily alum tanning but some chrome and vegetable tanning, received a demonstration grant in 1967 from the FWPCA to investigate and demonstrate methods of treating tannery wastes for discharge to a small stream. A research contract with Vanderbilt University produced findings which have previously been reported and are reviewed herein.

A modified completely-mixed activated sludge plant was constructed, along with facilities to handle specific problem wastes. After operating for a year, an EPA survey team conducted a study which showed that the plant was performing as predicted by the research phase, except for solids carryover from the secondary clarifier due to mechanical problems. After the problems were corrected, the plant began producing an effluent which more than met expectations, removing 97% of the suspended solids and 95% of the BOD. Due to conservation measures inside the tannery, however, the load on the plant is somewhat less than the design load, so the plant is operating as an extended aeration plant.

TABLE OF CONTENTS

	Page
ABSTRACT	iii
TABLE OF CONTENTS	v
LIST OF FIGURES	ix
LIST OF TABLES	xi
CONCLUSIONS	1
INTRODUCTION	3
BRIEF LITERATURE REVIEW	5
THE MANUFACTURING PROCESS	7
Wastewater Characteristics	9
Alum Tanning Process Waste Characteristics	9
Chrome Tanning Liquor Characteristics	12
Spent Vegetable Tanning Liquor	12
Alum Tanning Process Composite Characteristics	13
POLLUTIONAL LOAD	15
TREATMENT PROCESSES INVESTIGATED	17
Pretreatment	17
Sedimentation Studies	17
Spent Chrome Tanning Liquor Treatment	20
Spent Vegetable Tanning Liquor	22
Color Removal from Dye Wastes	27
Biological Treatment	29
Organic Content Reduction by Activated Sludge	31
Oxygen Requirements of Biological Unit	35
PROPOSED WASTE TREATMENT SYSTEM	37

Preceding page blank

TABLE OF CONTENTS (continued)

	Page
PROCESS DESIGN RECOMMENDATIONS	39
TREATMENT PLANT DESIGN	41
General Description of Waste Treatment Plant	41
Detailed Description of Plant Treatment Units and Design Criteria	42
Chrome Tanning Solution	42
Vegetable Tanning Liquor	42
Spent Dye Solutions	42
Screening and Equalization	43
Equalization Basin	43
Primary Clarifier	44
Aeration Basin	44
Final Clarifier	45
Sludge Concentration and Storage Tank	45
Lime Waste Storage	45
Nutrient Requirements	45
Laboratory Building	46
CONSTRUCTION AND STARTUP	47
EVALUATION OF PLANT PERFORMANCE	49
Water Flow	49
Summary of Plant Performance	50
BOD and COD Load	52
Organic Matter Removal	57
Solids	58
Nitrogen	60
Water Temperature	61
pH	61
Sulfides	62
Phosphorus	62
Dissolved Oxygen	62
Heavy Metals	63
Coliform Bacteria	64

TABLE OF CONTENTS (continued)

	Page
TREATMENT PLANT OPERATION	65
PLANT PERFORMANCE SINCE EPA SURVEY	67
ACKNOWLEDGEMENTS	71
REFERENCES	73

LIST OF FIGURES

No.		Page
1	ALUM TANNING PROCESS AT CALDWELL LACE LEATHER COMPANY	8
2	COD AND TURBIDITY OF SUPERNATANT AFTER LABORATORY SEDIMENTATION AS A FUNCTION OF pH	18
3	ZETA POTENTIAL OF SUPERNATANT AS A FUNCTION OF pH	18
4	SLUDGE INTERFACE SETTLING CURVE FOR ALUM TANNING PROCESS COMPOSITE WASTE	20
5	TOTAL CHROMIUM IN SUPERNATANT AS A FUNCTION OF pH	21
6	COLOR REMOVAL FROM SPENT DYE SOLUTION BY ACTIVATED CARBON	28
7	TWO FILL-AND-DRAW UNITS	29
8	CONTINUOUSLY FED ACTIVATED SLUDGE UNITS	30
9	OXYGEN UPTAKE OF UNACCLIMATED ACTIVATED SLUDGE FED TANNERY WASTES	31
10	COD REMOVED AS A FUNCTION OF LOADING	32
11	COD REMAINING AS A FUNCTION OF AERATION TIME	34
12	BOD OF INFLUENT AND EFFLUENT OF CONTINUOUS FLOW SYSTEM	34
13	OVERALL TREATMENT SCHEME PROPOSED FOR THE CALDWELL LACE LEATHER COMPANY	38

Preceding page blank

LIST OF TABLES

No.		Page
1	CHEMICAL CHARACTERISTICS OF ALUM TANNING PROCESS WASTES AT THE CALDWELL LACE LEATHER COMPANY	10-11
2	CHARACTERISTICS OF SPENT VEGETABLE TANNING LIQUOR	12
3	CHARACTERISTICS OF ALUM TANNING PROCESS COMPOSITE WASTES AT THE CALDWELL LACE LEATHER COMPANY	14
4	WEEKLY POLLUTIONAL LOAD FROM TANNING OPERATION	15
5	TOTAL DAILY WATER USAGE FEBRUARY THROUGH AUGUST 1967	16
6	EFFECT OF pH ON COLOR INTENSITY OF SPENT VEGETABLE TANNING LIQUOR	23
7	EFFECTS OF ACETONE TREATMENT OF SPENT VEGETABLE TANNING LIQUOR	23
8	TREATMENT OF SPENT VEGETABLE TANNING LIQUOR WITH ALUM TANNING SOLUTION	24
9	ANALYSIS OF VEGETABLE TANNING LIQUOR TREATED WITH ALUM TANNING LIQUOR	25
10	QUALITATIVE RESULTS OF SELECTED COMPOUNDS FOR COLOR REMOVAL FROM SYNTHETIC DYE MIXTURE	26
11	REMOVAL OF COLOR BY TWO ACTIVATED CARBON COLUMNS IN SERIES--RUN NO. 2	27
12	COMPARISON OF COD AND BOD VALUES	33
13	WATER FLOW DURING SURVEY	50
14	MEAN VALUES OF PARAMETERS DURING EPA SURVEY	51

Preceding page blank

LIST OF TABLES (continued)

No.		Page
15	BOD LOAD DURING SURVEY	52
16	COD LOAD DURING SURVEY	53
17	BOD LOADING RATES DURING SURVEY	54
18	COD LOADING RATES DURING SURVEY	55
19	ORGANIC MATTER REMOVALS DURING EPA SURVEY	58
20	SUSPENDED SOLIDS DURING EPA SURVEY	59
21	MEAN VALUES OF NITROGEN FORMS DURING EPA SURVEY	59
22	MEAN VALUES OF HEAVY METALS DURING EPA SURVEY	63
23	COLIFORM COUNTS DURING EPA SURVEY	64
24	PLANT PERFORMANCE IN 1972	67

CONCLUSIONS

This project showed that wastes from a small tannery using the alum tanning method principally, with small amounts of chrome and vegetable tanning, can be treated effectively, by adjustments of conventional methods, for discharge into a small stream without damage. The design of the completely mixed activated sludge plant was based on a laboratory pilot plant study, and the operating results of the full-scale plant closely duplicated the results of the laboratory study.

Results of a survey of the operation of the full-scale plant showed BOD removals of 93% and COD removals of 88%. Both would have been higher had not a problem with the sludge return system caused excessive solids carryover from the secondary clarifier during the survey.

Implementation of the recommendations of the EPA survey team and consultants resulted in improved operation during 1972. By mid-1972, SS reductions of 97% and BOD removals of 96% were being achieved.

INTRODUCTION

In 1967, the Caldwell Lace Leather Company, of Auburn, Kentucky, was awarded research and demonstration grant No. WPRD 25-01, by the Federal Water Pollution Control Administration, now part of the Environmental Protection Agency (EPA) to develop and demonstrate methods for the treatment of tannery wastes.

This tannery is unusual, and possibly unique, in that all three major tanning processes--chrome tanning, alum tanning, and vegetable tanning--are carried out at the same location. Thus, there was an opportunity to work with a wide variety of waste streams, and to determine the effect each would have on the waste treatment process. In addition to the actual tanning processes, the waste treatment plant would also be required to handle the wastes from the leather finishing operations, such as fat liquoring and dyeing.

Tannery wastes are not a large part of the overall pollution problem in the United States, but they can cause severe localized problems. Typically, tannery wastes are highly concentrated, both in terms of organic matter and inorganic ions; and the batch nature of the tanning process results in a waste stream which varies radically with time. These characteristics have made complete biological treatment of tannery wastes rare in the past.

It was anticipated that design parameters developed through this study would be applicable to the tanning industry in general. While previous work had been concentrated on pretreatment schemes, this study was to investigate and develop a treatment method for the tannery wastewaters so that they could be discharged directly into a small receiving stream.

The tannery is located on the bank of Black Lick Creek, a small stream which rises about 0.5 miles south of the town of Auburn. The stream then flows northward through the town and adjacent farmland for about three miles until it disappears in a series of sinkholes and enters the underground water streams which flow through the cavernous limestone which underlies most of central Kentucky.

The waste treatment plant of the City of Auburn is located directly across the creek from the tannery. When the municipal treatment plant was built, it was intended to serve the entire city, including the tannery. However, the design failed to take into account the particular characteristics and high strength of tannery wastes and was never able to operate satisfactorily. In an effort to eliminate the impact of the tannery on the treatment plant, the city began bypassing the tannery wastes directly into the creek.

Preceding page blank

When the impact of the tannery wastes on the stream was brought to the attention of the tannery officials by the Kentucky Health Department, they agreed to construct and operate their own waste treatment plant and applied to FWPCA for technical assistance because of the absence of available information on methods of complete treatment of tannery wastes. The research and development grant was the result of this appeal.

In the first phase of this project, the Caldwell Lace Leather Company awarded a contract to Vanderbilt University, of Nashville, Tennessee, to investigate the characteristics of the different waste streams and to develop treatment methods. This "research phase" of the project was completed in September, 1967, and the results were reported by Tomlinson, Thackston, et al. (1)(2).

The consulting firm of Howard K. Bell and Associates, of Lexington, Kentucky, was retained to design a treatment plant embodying the concepts and features recommended by the research team. The treatment plant design was approved by the Kentucky Department of Health and bids for construction were called for. Because of difficulties in construction unrelated to the treatment process or the plant design, completion of construction was delayed until December, 1970.

Difficulties in start-up were also encountered, and it was May, 1971, before the treatment plant began functioning smoothly. In November, 1971, a team from the EPA conducted a survey of operation of the treatment plant to determine the effectiveness of the treatment being provided.

This report will review the characteristics of the wastes generated by the tannery and associated operations, describe the research which led to the design of the treatment process, describe the process and treatment plant design, and report on the results being achieved by the treatment plant. It will serve as the final report to EPA on the demonstration grant. It will borrow heavily on the already published reports mentioned earlier for the research and design phases, on the design report of Howard K. Bell and Associates, and on the report of the EPA industrial waste survey team for the section on results being achieved.

BRIEF LITERATURE REVIEW

The brief survey of the literature presented here was originally conducted in 1967. Since then, several significant articles and reports have been published. However, these have not been included in this literature survey because they were not available to the researchers at the time the work was being done. Thus, this survey briefly outlines the state-of-the-art of tannery waste treatment at the time of conception of the treatment plant which is the subject of this report.

The effects of tannery wastewaters on receiving streams and treatment facilities have been of concern to the tanning industry and to sanitary engineers for many years, although significant progress in devising suitable treatment techniques has been minimal. There have been a number of review and summary type articles on tannery process description, wastewater characterization, and suggested treatment techniques (3) (4) (5) (6) (7) (8) (9) (10) (11). The data indicate that the wastes are highly variable in composition because of the nature of the tanning process. The most extensive description is possibly that of Masselli, Masselli, and Burford (6).

There are several types of tanning processes, and the use of any of the processes is considered an art, with each individual tanner developing his own procedure and processing solutions. The types of treatment used for tannery waste generally have been limited to screening, flow equalization, and plain sedimentation or chemical precipitation, followed by treatment combined with municipal wastewaters. The success of biological treatment processes has been limited because of the high BOD concentration of the wastes, the extreme variability with time, and the presence of toxic components in the wastes. In spite of an extensive literature search, little was found in the way of laboratory or design data for complete treatment schemes. However, the information uncovered is valuable as background and for defining the problem.

In addition to the general review type of article, the literature contains a large number of articles describing the treatment of tannery wastes in combination with municipal wastewaters. Typical published reports (12) (13) (14) (15) (16) (17) (18) (19) (20) (21) (22) indicate that the tannery wastewaters are amenable to combined treatment with municipal wastewater if the ratio of tannery waste flow to total flow does not exceed approximately 25 percent. Also, it has been emphasized that pretreatment of the tannery wastes, including hair and fleshings removal, neutralization, and/or equalization, is important for satisfactory operation of the combined plant. The disposal of sludge produced from the treatment of tannery washes is reported as being one of the major problems of tannery waste treatment. It does not dewater well and tends to clog vacuum filters. The high concentrations of inorganic ions tends to hamper

separate anaerobic digestion. Since the purpose of this study was to develop methods for treating tannery wastes alone, this portion of the literature was not pursued extensively.

Parker (23) reported on the use of spray irrigation for the disposal of the wastewaters from a large tannery which used the vegetable tanning process. Once operating problems were overcome, the process apparently was successful in disposing of the wastes without nuisance. However, large amounts of land are required for this method.

Studies also have been conducted on possible methods of treatment of selected waste streams from a tannery. For example, Berg et al. (24) investigated the use of manganese for the precipitation of sulfides from beam-house wastes. Also, other physical and chemical methods have been investigated for suspended solids and biochemical oxygen demand removal from tannery wastewaters employing the chrome tanning process. Sproul et al. (25) (26) reported good reductions in BOD and suspended solids by using the spent chrome liquors as coagulants. The use of organic polyelectolytes also was investigated.

The references mentioned in this brief literature survey are only a portion of the total articles published in the worldwide literature. Eye and Graef (27) published a bibliography of 245 articles relating to tannery effluents. It is interesting to note that many of the articles first were published in European journals, thus indicating the geographical extent of the interest in treatment of wastewaters from tanneries.

THE MANUFACTURING PROCESS

The leather production facilities at Caldwell Lace Leather Company generally could be described as typical of a small tannery. The manufacturing processes are conducted by use of conventional lime pits, fleshing and unhairing machines, rotary drums, and rocker vats (for vegetable tanning). Approximately 85 percent of the leather production at this plant at the time of the study was by the alum tanning process, with chrome-tanned leather and vegetable-tanned leather accounting for approximately equal fractions of the remaining 15 percent.

The green salted hides first are soaked in three separate changes of water for a total of 24 hours to wash off the extraneous dirt, salt, and manure. They then are placed in a lime solution for seven days to loosen the hair and swell the hides. Small quantities of sulfides also are added to aid in this process. Each lime pit is used twice before discharge.

On removal from the lime pits, the hides are passed through successive machines for removal of hair and flesh particles. The hides then are washed in a continuous stream of water for about 30 minutes to remove the excess lime. To remove the remaining lime and the soluble proteinaceous material, the hides are placed in a rotating drum containing ammonium chloride and an enzymatic compound containing trypsin. After two hours in this "bating" solution, the hides are rinsed again.

Up to this point, the hides have all recived essentially the same treatment. Afterwards, the treatment varies with the type of tanning.

The hides slated to undergo alum tanning are pickled in an acid and sodium chloride solution in a rotating drum and the alum solution then is added directly to the drum. After tanning, the hides are split and shaved to uniform thickness, and sent to the dyeing plant. Since the alum tan is not water resistant, the dyeing must take place in an alum tan solution. Oils and fats then are added and the hides taken out and allowed to dry. Figure 1 is a schematic of the alum tanning process.

The chrome tanning process is similar to the alum tanning process except the pickling solution is slightly different. Chromium sulfate is used as a tanning agent instead of alum, and a re-tan is not necessary during dyeing.

In the vegetable tanning process, the hides are soaked in vats containing solutions of bark extracts and synthetic tanning agents for about five weeks before washing and dyeing. The waste discharge from this process is relatively small, but quite troublesome because of very high solids content, color, and COD.

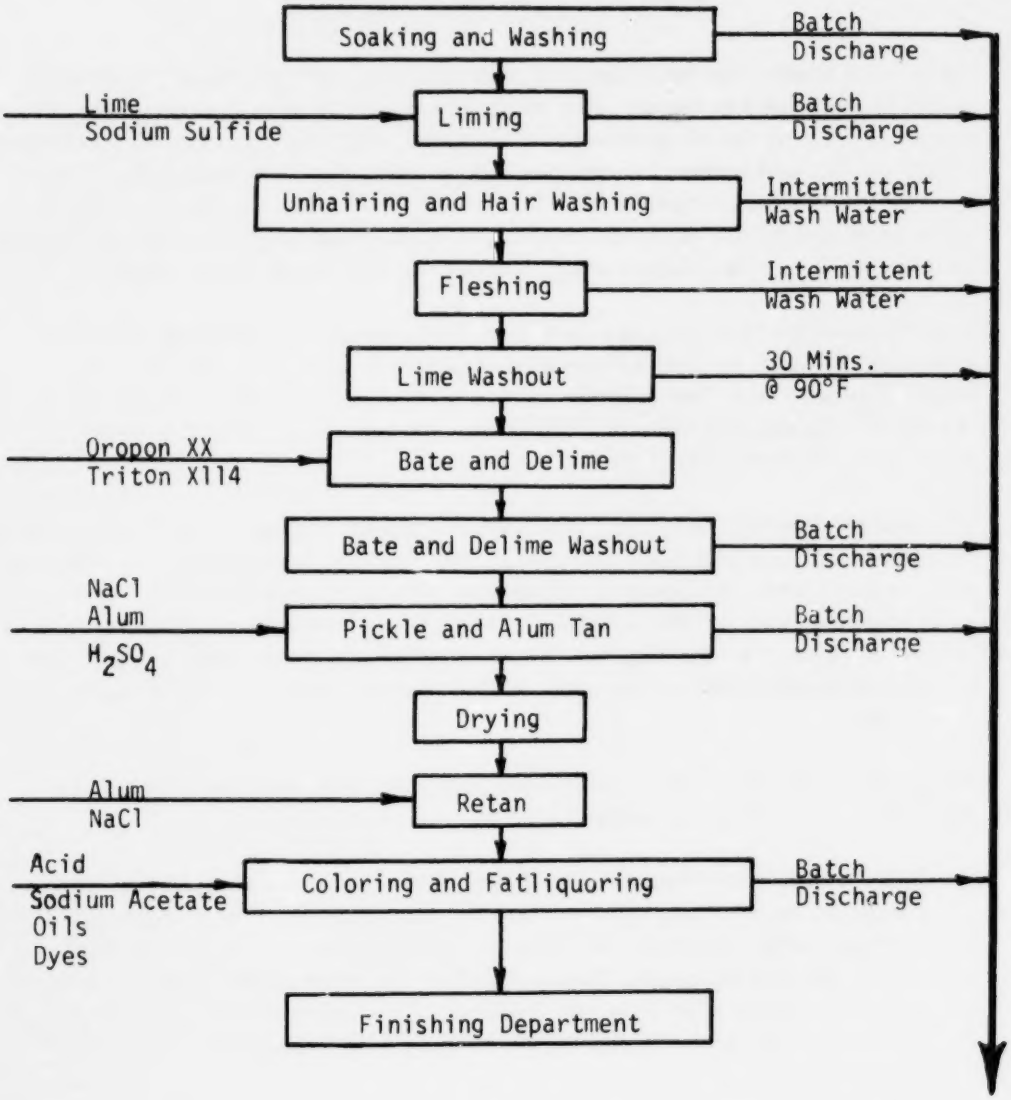

FIGURE 1 - ALUM TANNING PROCESS AT CALDWELL LACE LEATHER COMPANY

Studies of water-use records for a two-month period revealed that the average total water use was 520 gal/100 lb (2,200 l/100 kg) of hides processed. The processes contributing the most wastewater were the de-lime and bate wash, the lime wash, and the soak. The processes contributing the greatest pollution load, in terms of COD, were the lime pits discharge, the de-lime and bate wash, the spent dye solution, and the spent vegetable tanning liquor.

Wastewater Characteristics

Considerable effort was expended during the project to analyze the different types of wastewater emanating from the tannery.

The samples collected included grab samples from each major process step, composite samples of total alum tanning process wastes, and a weekly composite from the effluent of the existing holding tank. Other samples were collected at selected times and locations to aid in the overall evaluation of the wastewater problem. The alum tanning process composite wastewater samples were prepared by collecting spent liquors from the various operations and combining the different wastes on the basis of the quantity of the flow discharged from each process.

Alum Tanning Process Waste Characteristics

The average pollutional characteristics of the waste streams from the individual operations in the alum tanning process (Table 1) differ widely.

The wastewater from the lime pit is basically a lime-saturated solution containing undissolved lime, hair, and dissolved proteinaceous material, and represents the waste with the highest COD. The high neutralizing capacity of this waste can be used to good advantage in the overall treatment scheme. Although the pH of the composite sample from the lime washout operation was high (11.2), chemical analysis and the electrometric titration curves indicated that the caustic alkalinity and buffering capacity of this waste stream was limited.

The wastewater from the pickling-alum tanning solution can be described best as an acidic salty solution of aluminum sulfate containing considerable quantities of dissolved organic material. The electrometric titration curve for the spent pickling-alum tanning solution suggested that the high mineral acidity of this waste stream could be used to reduce the alkalinity of the wastes from the previous processes by combining the waste streams.

TABLE 1 - CHEMICAL CHARACTERISTICS OF ALUM TANNING PROCESS WASTES AT THE CALDWELL LACE LEATHER COMPANY *

Parameter	Washing and Soaking	Lime Pit Discharge	Lime Washout	Bate and Delime Washout	Spent Alum Tanning Liquor	Spent Dye Solution
Conductivity, micromhos/cm	13,800 -	27,000 -	2,600 -	4,400 -	60,000 -	- -
pH	7.2 6.8-7.4	12.1 11.9-12.3	11.1 10.9-11.3	8.8 8.7-8.9	3.3 3.2-3.6	3.4 -
Phenolphthalein Alkalinity, mg/l as $Ca\ CO_3$	- -	4,980 3,810-6,150	180 130-225	160 130-190	- -	- -
Total Alkalinity, mg/l as $CaCO_3$	215 140-295	6,240 4,970-7,500	380 335-430	460 430-480	- -	- -
Mineral Acidity, mg/l as $CaCO_3$	- -	- -	- -	- -	13,400 9,000-20,200	9,600 -
Total Acidity, mg/l as $CaCO_3$	25 0-40	- -	- -	- -	22,100 20,000-27,400	17,200 -
Chlorides, mg/l as Cl^-	5,100 2,590-8,250	11,980 8,350-15,600	580 530-630	940 710-1180	33,160 24300-38700	25,480 25250-25700
Total Hardness, mg/l as $CaCO_3$	210 -	6,480	280 -	540 -	- -	- -

*Values tabulated are averages with range underneath

TABLE 1 - CONTINUED

Parameter	Washing and Soaking	Lime Pit Discharge	Lime Washout	Bate and Delime Washout	Spent Alum Tanning Liquor	Spent Dye Solution
Total Solids, mg/l	-	-	-	-	109,800	-
	-	-	-	-	-	-
Fixed Solids, mg/l	-	-	-	-	54,630	-
	-	-	-	-	-	-
Suspended Solids, mg/l	-	-	-	-	1,720	-
	-	-	-	-	-	-
COD, mg/l	1,190 925-1670	11,720 9760-13,800	800 780-830	1,620 1600-1640	5,400 2750-7300	5,330 5050-5610
BOD, mg/l	-	-	-	-	2,750	5,000
	-	-	-	-	-	-
Ammonia Nitrogen, mg/l	26	169	15	358	456	-
Organic Nitrogen, mg/l	12	168	12	26	15	-
Total Phosphate, mg/l	8	3	7	4	6	-

The spent dye solution for the alum tanning operations is basically the same as the alum tanning solution, with the addition of dyes and oils. The only other difference is that somewhat smaller quantities of salt and acidic compounds are used in the preparation of alum tanning dye solution.

Chrome Tanning Liquor Characteristics

The spent chrome liquor contained between 400 and 600 mg/l of chromium, had a COD of 4,300 mg/l, and had a chloride content of 72,000 mg/l. The pH of the spent chrome tanning liquor ranged between 3.5 and 4.5, and had a characteristic light blue color. The characteristics of the wastes from the coloring operation following chrome tanning were essentially the same as those from the coloring operation following alum tanning, except for the lack of alum. The ratio of pounds of chrome tanned hides to gallons of spent chrome liquor was about 10 to 1.

Spent Vegetable Tanning Liquor

A sample of the spent vegetable tanning liquor was obtained as it was discharged from the last vat (No. 5) to the plant sewer. Chemical analyses of this discharge (Table 2) show that the solution is essentially a colloidal suspension of the bark extracts, which are largely tannins.

TABLE 2 - CHARACTERISTICS OF SPENT VEGETABLE TANNING LIQUOR

Characteristic	Concentration
Suspended solids, mg/l	1,840
Total solids, mg/l	76,600
Total volatile solids, mg/l	24,000
Total fixed solids, mg/l	52,600
Chemical oxygen demand, mg/l	51,600
5-Day BOD, mg/l	2,500
Ultimate BOD, mg/l	7,500
pH	5.0
Color, Caldwell color units	95

The color of the spent vegetable tanning liquor is different in hue and tint from the commonly-used platinum-cobalt standards, making comparison with the standards difficult. Therefore, the optical density of the solution was measured with a spectrophotometer at a wavelength of 420 mμ and converted to "Caldwell Color Units" by use of a standard curve. Twenty Caldwell color units have an optical density of 0.56.

Alum Tanning Process Composite Characteristics

Since this tanning process results in a series of batch discharges throughout the operating day, it was decided to collect samples of wastewater from each operation and prepare composite process samples, based on the daily volume of waste discharged from each operation. One disadvantage of the method of compositing employed was that wastewater resulting from floor washings was not included in the final composite. The overall net effect of this method of sampling was to obtain composite samples in which the concentration of pollutants would be somewhat higher than if they had been collected from the total plant effluent, since comparison with the process wastes showed that the floor washings were relatively free of pollutants. However, the weight of pollutants discharged could be assumed to be approximately the same as would be obtained from the plant effluent.

Later laboratory studies indicated that color removal by biological treatment was not effective. Therefore, composite samples were prepared with and without the spent dye solutions. Characteristics of the composite samples are presented in Table 3.

The different composite samples prepared varied during the course of the study because they were prepared from different batch discharges. The major differences among the composite samples were in the variables pH, alkalinity, and acidity because of the highly variable characteristics of the lime pit discharges. The organic content as measured by chemical oxygen demand was relatively unchanged at approximately 3,000 mg/l, and the biochemical oxygen demand of the composite samples was relatively stable at from 22 to 35 per cent of the chemical oxygen demand.

TABLE 3.--CHARACTERISTICS OF ALUM TANNING PROCESS COMPOSITE WASTES AT THE CALDWELL LACE LEATHER COMPANY

Parameter	Sample	
	Alum Composite Including Spent Dye	Alum Composite Excluding Spent Dye
Conductivity, micromhos/cm	-	11,000
pH	4.9-8.0	5.5-8.5
Phenolphthalein Alkalinity mg/l as $CaCO_3$	-	605
Total Alkalinity, mg/l as $CaCO_3$	-	1,080
Mineral Acidity, mg/l as $CaCO_3$	none	none
Total Acidity, mg/l as $CaCO_3$	300-400	none
Chlorides, mg/l as Cl^-	4,700	3,600
Total Hardness, mg/l as $CaCO_3$	-	1,630
Chemical Oxygen Demand, mg/l	3,050	2,950
Total Solids, mg/l	-	10,430
Total Fixed Solids, mg/l	-	7,760
Ammonia Nitrogen, mg/l	196	145
Organic Nitrogen, mg/l	43	47
Total PO_4^{-3}, mg/l	-	5.2
Biochemical Oxygen Demand 5-day, 20°C, mg/l	750-1050	650-950

POLLUTIONAL LOAD

The pollutional load from the tanning operation is highly variable throughout the operating day. Since both the wastewater characteristics and the flow vary with individual steps in the operation, the pollutional load discharged per unit of time throughout the day will not characterize the waste. Also, some units are discharged only two or three times weekly. These factors make pollutional load expressed on a daily basis unrealistic. The shortest time interval in which the tanning operations are normally repetitive is one week. Although the tannery works a five-day week, the flow must be fed to the biological treatment units over a seven-day week. This fact, plus the need to reduce the impact of batch discharges, will make equalization necessary. Therefore, the pollutional load from each operation is expressed in Table 4 on a weekly basis.

TABLE 4--WEEKLY POLLUTIONAL LOAD FROM TANNING OPERATIONS

Process	Flow (gal/week)	Chemical Oxygen Demand (lbs/week)	Alkalinity as $CaCO_3$ (lbs/week)	Total Acidity as $CaCO_3$ (lbs/week)	Chlorides (lbs/week)
Soak	24,000	190	45	7	1020
Lime Pit Discharge	7,500	725	390	None	750
Lime Wash	30,000	200	95	None	-
Delime & Bate Wash	40,000	540	150	None	313
Spent Alum Solution	3,000	135	-	550	830
Spent Dye Solution	6,000	265	-	860	1275
Spent Vegetable Liquor	600	258	None	-	-
Spent Chrome Liquor	600	20	None	85	360
TOTAL	111,700	2333	680	1502	4548

The volumes of wastewater discharged from the tannery were determined by daily records of total water used at the plant. Records of total daily flows and hourly water usage that were kept from February through August of 1967 were reviewed and were used for this project. Water used for tanning operations was obtained from Black Lick Creek and was coagulated and settled prior to use.

The mean, median, minimum,and maximum daily water usages are presented in Table 5. It is of interest to note that the variation of daily mean flows during the week is less than 5,000 gallons. This is significant when determining the economical size for the equalization basin. The ratio of maximum flow to the mean flow for a particular day of the week varied from 1.38 (Thursday) to 1.57 (Wednesday), and the ratio of the maximum day to the minimum day was 2.45. Although the extreme variation was from 20,155 to 49,900 gallons per day, 80 percent of the flows were between 25,000 and 40,000 gallons per day. Over the period of record, the plant averaged 520 gallons of water for each 100 pounds of hides processed.

TABLE 5--TOTAL DAILY WATER USAGE
FEBRUARY THROUGH AUGUST, 1967

Day of Week	No. of Observations	Flow in Gallons per Day			
		Mean	Median	Minimum	Maximum
Monday	28	34,300	32,900	26,100	49,360
Tuesday	29	32,100	30,225	24,085	49,900
Wednesday	29	31,300	29,155	23,900	47,720
Thursday	29	33,000	32,700	25,900	45,610
Friday	21	29,500	28,240	20,155	41,100

TREATMENT PROCESSES INVESTIGATED

Based on the literature review, water-use records, and wastewater characteristics, tannery waste treatment plants should include certain units or processes. The following operations were considered during this study:

1. Screening.
2. Flow equalization.
3. pH adjustment.
4. Primary sedimentation.
5. Biological treatment and secondary sedimentation.

In addition to the major elements listed above, it was determined that certain waste streams should receive special treatment before being discharged to the equalization basin. These were:

1. Spent chrome tanning solution.
2. Spent vegetable tanning solution.
3. Spent dye solutions.

Pretreatment

Field studies showed that 80-mesh vibrating screens effectively screened hair, fleshings, and leather bits from the tannery's wastewater. However, clogging was evident and a self-cleaning arrangement would be necessary. Clogging was less severe when a 200-mesh screen was used.

Sedimentation Studies

For the sedimentation studies, a composite sample of wastes from the alum tanning process was adjusted to various pH values with either lime or sulfuric acid. The pH-adjusted samples were flash mixed and allowed to settle for one hour. The resulting supernatants then were analyzed for turbidity and COD (Figure 2). Optimum pH for coagulation and sedimentation was found to be 6.7. One hour of sedimentation removed about 71 percent of the COD at pH 6.7 and about 64 percent at the original pH.

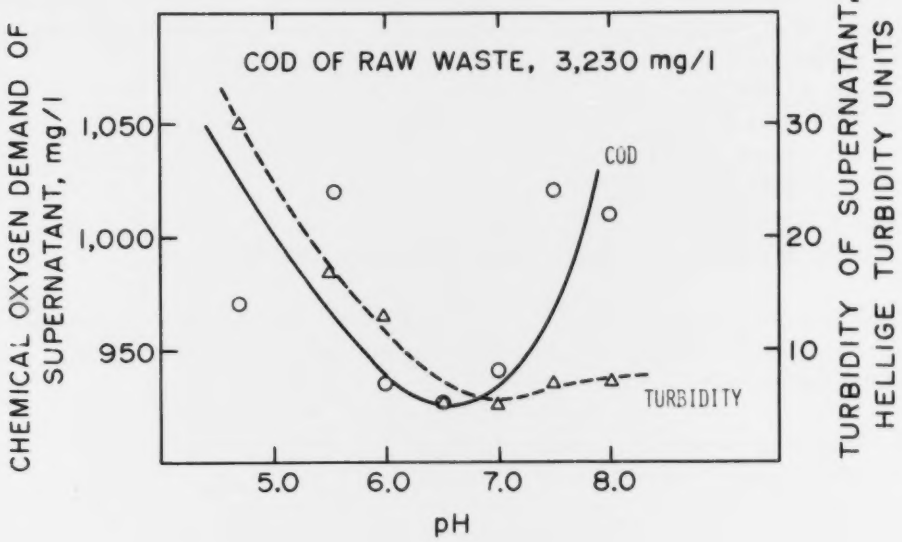

FIGURE 2--COD AND TURBIDITY OF SUPERNATANT AFTER LABORATORY SEDIMENTATION AS A FUNCTION OF pH

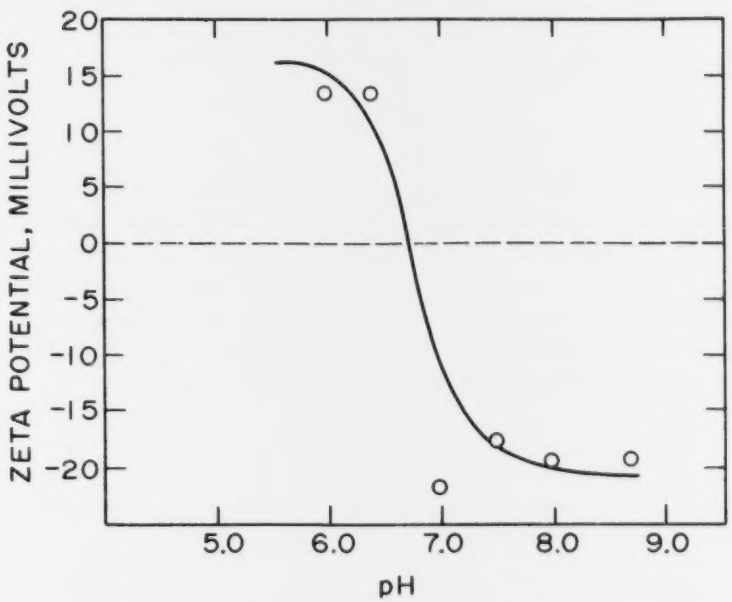

FIGURE 3--ZETA POTENTIAL OF SUPERNATANT AS A FUNCTION OF pH

The large amount of alum remaining in the spent alum tanning solution, combined with the lime from the lime pit discharge, resulted in a noticeable floc being formed in the alum tanning process wastewater composite. Ferric chloride and alum were added in increasing dosages but neither produced any obvious improvement in the floc characteristics. The addition of cationic polyelectrolytes was found to be even less effective than additional alum or ferric chloride.

The zeta potential of the particles in the various supernatants also was determined. A plot of these data (Figure 3) suggests that the optimum turbidity removal at pH 6.7 is due primarily to charge neutralization.

Floc formation was evident when the pH of the alum tanning process wastewater composite sample was adjusted to 6.7. However, the floc formed was light and fluffy, and might be resuspended by sludge removal facilities within the sedimentation basin.

Anionic polyelectrolytes were found to be effective coagulant aids, which agreed with the findings of Eye and Graef (29). Six mg/l of Nalco-675, an anionic polyelectrolyte, were added to the raw waste and, after 30 minutes of settling, the supernatant had a COD of 800 mg/l, approximately 15 percent less than that obtained without polyelectrolyte. Even more important, the floc was dense and tough, and resettled rapidly when disturbed. It was further determined that increasing the dosages of polyelectrolyte did not significantly improve the floc properties. The anionic polyelectrolyte, DOW-A-22, was found to have about the same effect as Nalco-675 and at approximately the same dosage.

Surface loading rates were determined for a sedimentation basin receiving the wastewater, which had been adjusted to a pH of 6.7, using the method outlined by Rich (28). A one-liter graduated cylinder was filled with the pH-adjusted waste and the location of the supernatant-sludge interface was determined at various times (Figure 4). The suspended solids concentration in the settled sludge was 7,300 mg/l. The surface loading rate was calculated to be 750 gal/day-sq ft with a detention time of 1.5 hr. The resulting supernatant had a COD of about 925 mg/l and a total suspended solids concentration of about 150 mg/l.

At a pH of 6.7 and a dosage of 6 mg/l of Nalco-675, the surface loading rate was calculated to be 860 gal/day-sq ft. Therefore, the use of the anionic polyelectrolyte increased the permissible sedimentation basin surface loading rate.

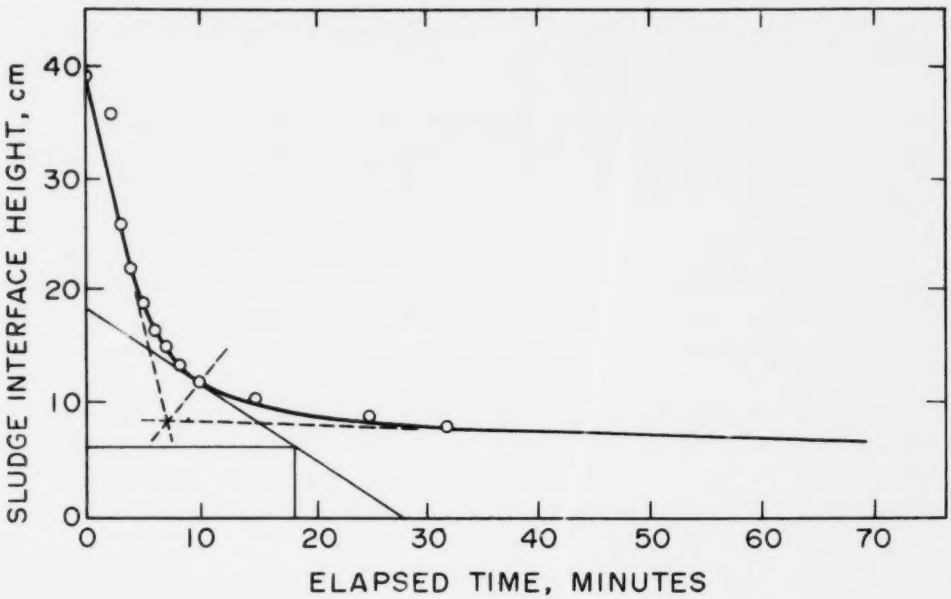

FIGURE 4 - SLUDGE INTERFACE SETTLING CURVE
FOR ALUM TANNING PROCESS COMPOSITE WASTE

Spent Chrome Tanning Liquor Treatment

The spent chrome tanning liquor is a concentrated, acidic solution containing a high concentration of chromium, chlorides, and other contaminants. Its characteristics make it desirable to pre-treat this relatively small quantity of waste prior to discharge into the total waste stream. One commonly used method of chromium removal is conversion of all chromium to the trivalent form and then precipitation of the trivalent ions as chromium hydroxide. As the chromium ions in the spent chrome tanning solution are already in the trivalent form, removal of the chrome can be accomplished by pH adjustment and sedimentation.

The results of the lab tests (Figure 5) show that optimum removal of chromium from the spent chrome liquor was attained at a pH of 11.5, in this study, although a pH of 9.5 produced results almost as good.

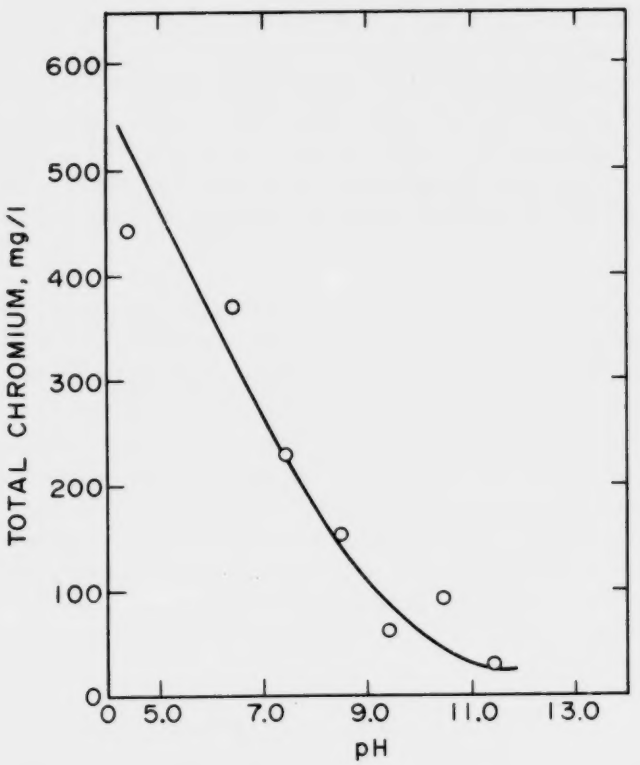

FIGURE 5 - TOTAL CHROMIUM IN SUPERNATANT AS A FUNCTION OF pH

Observations also were made on the settleability of precipitated chrome sludge. A surface loading rate of approximately 200 gal/day-sq ft was calculated using the procedure outlined by Rich (28). The detention time under the conditions of the test should be at least four hours. Suspended solids concentrations were 1,530 mg/l and 22,000 mg/l in the pH adjusted waste and in the sludge, respectively. After approximately 4 hours of sedimentation, the supernatant had a total chrome content of 25 mg/l and a COD of about 3,000 mg/l. After 21 hr of sedimentation, the chrome content was 6 mg/l. The chrome content of the final waste discharge will be much less

after it is diluted with the other plant wastes, and the concentration in the receiving stream will be negligible.

Spent Vegetable Tanning Liquor

Although the volume of this waste is not large, even at a vegetable tannery (about ten percent of total flow), it represents a large fraction of the pollutional load because of its strong concentration. The BOD and COD are not removed easily by biological waste treatment because of the nature of the tannin molecules, and there is some toxic effect. Also, the color, which is intense, is not removed by biological waste treatment. This suggests that this waste should be treated separately to remove the tannin colloids which cause the high COD and color before it is discharged to the equalization basin.

The effect of pH on the color intensity of the spent vegetable tanning liquor was established by color observations at various pH levels (Table 6). pH has a pronounced effect on the color of this waste, especially in the alkaline range. Also, it was found that the color intensity declined with the addition of acid, but that the color returned to the same level with readjustment of pH. Dosages of granular activated carbon up to 5,000 mg/l were used in the preliminary color removal tests with no detectable reduction in the color, even with contact times up to 20 hr. From a qualitative standpoint, "massive" dosages of carbon will reduce the color somewhat. However, this possibility of treatment for color removal from spent vegetable tanning liquor was not investigated further because of the excessive dosages required for very limited color removal.

The method of removal of lignin from pulp mill black liquor as developed by Woodward and Etzel (30) was investigated as a means of treatment of the spent vegetable tanning liquor. Briefly stated, the method requires equal additions of waste and solvent, pH adjustment, slow mix, and sedimentation. The supernatant is decanted, vacuum distilled for removal of solvent, and treated with 35-percent hydrogen peroxide in a waste-to-peroxide volume ratio of 10-to-1. Etzel reported that the best results were obtained by using acetone as the solvent.

Samples of the spent liquor and acetone were mixed in ratios of 9-to-1, 2-to-1, and 1-to-1, adjusted to pH 12 with sodium hydroxide, and slowly mixed for 15 min.

TABLE 6 - EFFECT OF pH ON COLOR INTENSITY OF SPENT VEGETABLE TANNING LIQUOR

pH	Color Intensity (Caldwell color units)
5.0*	95
6.0	127
7.0	187
8.0	380
9.0	490
10.0	1,000
12.0	1,960

*Original pH of sample

TABLE 7 - EFFECTS OF ACETONE TREATMENT OF SPENT VEGETABLE TANNING LIQUOR

Ratio of Vegetable Tan Liquor to Acetone	Appearance after 16-hr Contact Time
9:1	No Floc
3:1	Both settleable and floating solids
1:1	Approximately 25 percent of total volume is settled sludge; good separation

The most promising results were obtained with a one-to-one ratio of waste to acetone (Table 7). However, from an operating standpoint, recovery of the acetone would be necessary for the process to be economical. Other treatment techniques which would be more applicable to tannery wastes then were investigated.

The spent alum tanning solution also was evaluated for treatment of the spent vegetable tanning liquor. Tests using spent alum as the coagulant were conducted with some observations on sludge settling rates and total sludge production (Table 8).

Results of selected chemical analyses of the supernatant from the alum treatment are presented in Table 9. The parameters of particular significance--color and suspended solids--are reduced markedly although the COD reduction primarily is because of dilution and the reduction in color is partially due to the reduction in the pH. The reduction in the other parameters was not as significant.

TABLE 8 - TREATMENT OF SPENT VEGETABLE TANNING LIQUOR WITH ALUM TANNING SOLUTION*

Settling Time (min)	Ratio of Vegetable Tan to Spent Alum Solution		
	4:1	2:1	1:1
0	200†	200†	200†
10	150	180	200
20	90	160	180
45	60	130	160
60	55	120	145
1,080	30	50	70

*Results tabulated as height of supernatant-sludge interface in ml.

†Total volume of waste plus alum.

TABLE 9 - ANALYSIS OF VEGETABLE TANNING LIQUOR TREATED WITH ALUM TANNING LIQUOR

Parameter	Ratio of Vegetable to Alum Tanning Liquor		
	4:1	1:1	Raw Waste
pH	3.5	3.35	5.0
Total solids, mg/l	73,760	71,510	76,600
Total vol. solids, mg/l	31,400	31,560	24,000
Suspended solids, mg/l	1,260	30	1,840
COD, mg/l	41,800	27,900	51,600
Color, Caldwell color units	90	38	120
SS in sludge, mg/l	23,820	12,800	--

Further reductions in color content should be produced by adjustment of the pH to approximately seven. This would enhance greatly the production of an insoluble aluminum hydrous oxide floc, adding the effects of orthokinetic flocculation to the perikinetic coagulation.

It should be noted that the sludge in the four-to-one vegetable to alum tanning liquor solution settled much faster than that resulting from the equal volumes of vegetable to alum tanning liquor. A settling period of 16 to 18 hr would be required to produce the above sludge densities if a ratio of 1-to-1 were used; while only 2 to 4 hr are needed for the 4-to-1 ratio. However, the quality of the effluent resulting from the longer settling time would justify the use of a one-to-one ratio for this particular installation where the volume of vegetable tanning liquor is small.

Studies of the use of NaOCl as an oxident showed that massive doses were required to reduce the color of the spent vegetable tanning liquors appreciably. Doses of free available chlorine of 8000 mg/l, and detention times of 2 to 4 hours were necessary to effect color removal. This treatment was not considered economical.

Some investigators have found that lime is an effective coagulant for spent vegetable tanning liquors, but repeated trials with the liquors used in this study produced no beneficial results. The result of lime addition was only to produce a very turbid, muddy-looking solution and no settleable sludge. Filtration of this solution did not remove the color. Because all vegetable tanning solutions are different, however, lime coagulation may be successful in some instances, and this process should be investigated in every case.

TABLE 10 - QUALITATIVE RESULTS OF SELECTED COMPOUNDS FOR COLOR REMOVAL FROM SYNTHETIC DYE MIXTURE

Compound	Test Condition	Results*			Comment
		1	2	3	
Stannous chloride	Basic solution (NaOH)	X			Colored ppt formed
Stannous chloride	Acid medium (HCl)	X			
Sodium meta-bisulfite	Aqueous dye solution			X	
Sodium meta-bisulfite	Acidic			X	
Sodium meta-bisulfite	Basic			X	
Zinc-dust	pH 9.0 1-hr contact time	X			Small amount ppt
Hydrazine chloride	Basic media		X		
Hydrazine chloride	Acidic media		X		
Sodium hypochlorite	Aqueous dye solution		X		High dosages
Sodium sulfite	Acidic media			X	
Potassium permanganate	Acidic media	X			pH 3, and sodium meta-bisulfite to reduce excess KMnO

*Results by Appearance: 1 - Color removal completely; 2 - Color intensity decreased; 3 - No obvious change.

After the completion of the research phase of this project, a later project developed an effective method of removing the color from spent vegetable tanning liquors, but this method was not available when the treatment plant described in this report was designed. Briefly, the process involves the addition of acid to lower the pH of the solution to the isoelectric point of 2.0 to 2.5, and the addition of a high molecular weight cationic polyelectrolyte to coagulate the colloidal solution.

Color Removal from Dye Wastes

The color in the spent dye wastes was not removed or diminished by biological waste treatment. Selected chemicals were investigated as pretreatment processes for the dye wastes prior to biological treatment (Table 10). Because of the large dosages necessary to effect color removal, this route was not pursued extensively.

Considerable work then was done using adsorption on activated carbon to remove the color. This approach generally was successful, although large quantities of carbon and low application rates were necessary. Regeneration of the carbon by elution with acid and alkali were unsucessful.

TABLE 11 - REMOVAL OF COLOR BY TWO ACTIVATED CARBON COLUMNS IN SERIES--RUN NO. 2

Cumulative Flow (ml)	Ratio of Effluent Color to Spent Dye Color
110	0
320	0
530	0
740	0
1,060	0.015
1,370	0.022
1,630	0.033
1,955	0.042
2,215	0.055
2,640	0.082
2,850	0.134
3,160	0.178
3,345	0.254

Note: Flow rate = 0.5 gpm/sq ft; color in dye composite = 60 Caldwell color units.

Breakthrough of color was quite rapid, even at an application rate of 0.5 gpm/sq ft. Consequently, columns in series were tried with considerably better results. The results of a test using two columns in series are presented in Table 11. Each column contained 3.5 g of fine carbon and 2.0 g of coarse carbon (as a filtering material to prevent clogging of fine carbon).

Since clogging of the fine might be a problem, a test was run to evaluate the relative effectiveness of fine and coarse carbon. The color removal capacity of the fine carbon was approximately five times that of the coarse carbon (Figure 6).

The results show that dye adsorption is relatively slow, and that columns in series or a deep bed should be used.

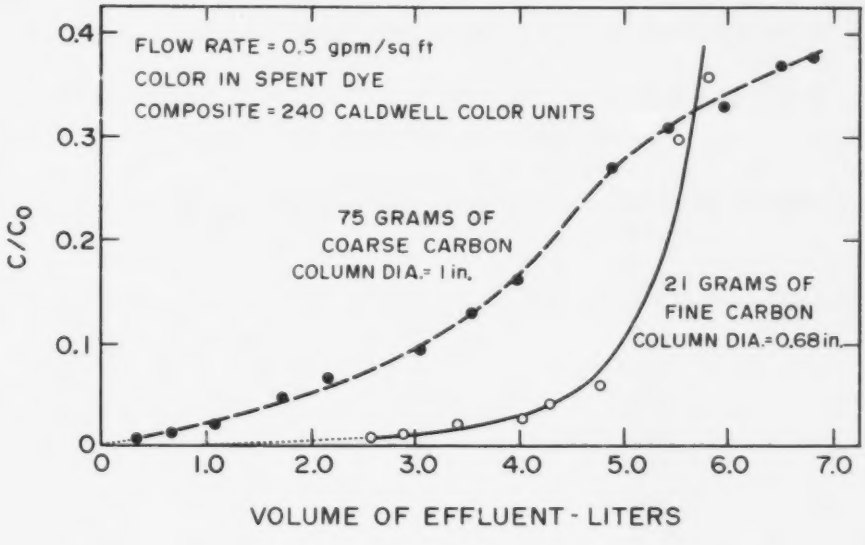

FIGURE 6 - COLOR REMOVAL FROM SPENT DYE SOLUTION BY ACTIVATED CARBON

Biological Treatment

Both trickling filters and stabilization ponds have been tested or recommended in the past for the treatment of tannery wastes. However, trickling filters tend to become coated with grease and/or precipitated calcium carbonate from the beamhouse wastes. Also, ponds require large land areas--not available in this instance nor in many tanneries. Consequently, biological treatment studies were conducted utilizing the activated sludge process.

A completely mixed system was used in the lab studies and was recommended for the treatment plant. Completely mixed systems are more stable, easier to operate, and help to dilute and alleviate shock or load variations on the biological system. Preliminary work indicated that a conventionally loaded system would be satisfactory.

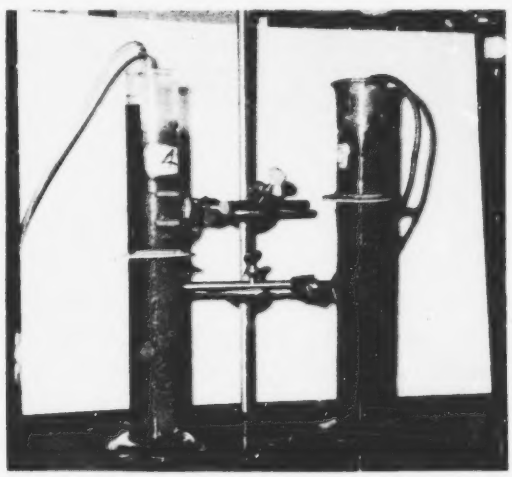

FIGURE 7 - TWO FILL-AND-DRAW UNITS

Four laboratory scale biological units (Figures 7 and 8) were employed in the studies. Two were continuous-flow units using settled alum tanning process composite wastes as feed (including spent dye) and two were fill-and-draw units, with 23 hr of aeration and 1 hr of sedimentation. One fill-and-draw unit used alum tanning process composite waste with dye solution, and the other unit employed alum tanning process composite wastes,

FIGURE 8 - CONTINUOUSLY FED ACTIVATED SLUDGE UNITS

without the spent dye solution. After it became apparent that the dye color was not being removed by biological treatment, feed without the dye was used. The waste was screened, adjusted to pH 6.7, and settled for 2 hr before being fed to the biological treatment units.

As a preliminary step, the oxygen uptake rate of sludge from the Franklin, Tennessee, municipal plant was measured, after the addition of several tannery waste concentrations, to determine the general toxic effects of the tannery wastes to unacclimated sludge. The results (Figure 9) indicate no toxic effects in the concentrations studied. As the total plant composite was used, all of the waste streams were represented, including the vegetable tan liquor, the chrome tan liquor, and the dye wastes.

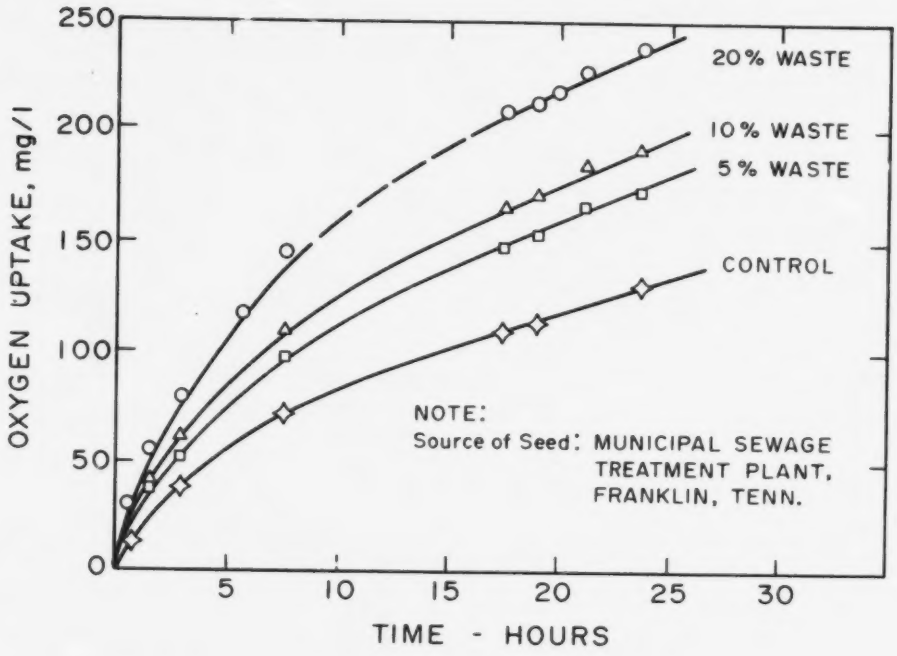

FIGURE 9 - OXYGEN UPTAKE OF UNACCLIMATED ACTIVATED SLUDGE FED TANNERY WASTES

Organic Content Reduction by Activated Sludge

The effluent from all laboratory activated sludge units was collected and analyzed, and the organic content reduction in terms of COD was calculated. The effluent COD was run on an unfiltered sample, since this represents the total organic load discharged to a receiving stream (Figure 10). Approximately 65 percent of the COD was removed up to a loading rate of 0.9 lb COD/day-lb of MLVSS. At higher loading rates, the efficiency declines somewhat. This loading rate is approximately equal to 0.55 lb/day-lb on a BOD basis.

The COD of the effluent was generally 400 to 500 mg/l with few exceptions even though the applied load varied. While this is quite high, it includes much non-biodegradable organic matter. Table 12 presents the results of simultaneous BOD and COD tests on the waste at various stages and shows

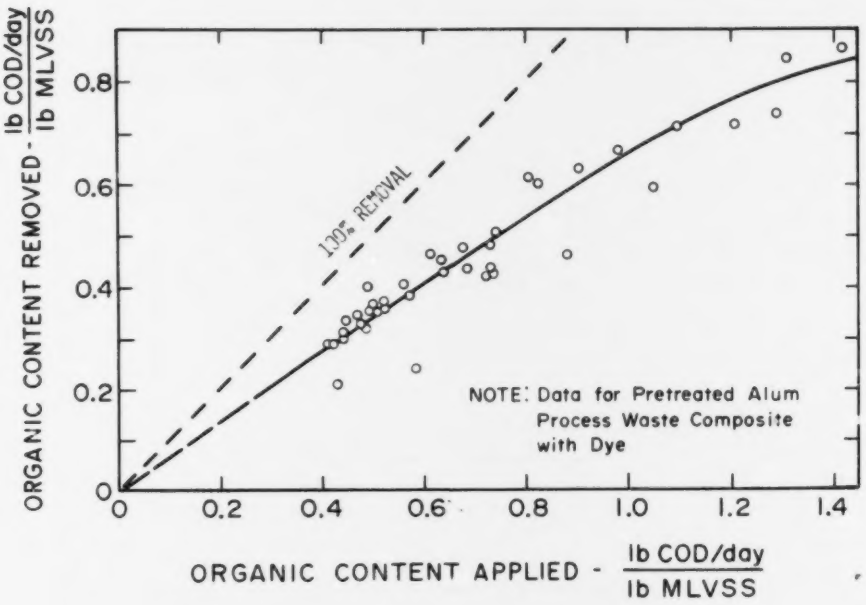

FIGURE 10 - COD REMOVED AS A FUNCTION OF LOADING

that the BOD/COD ratio is much lower on the effluent than it is on the influent to the biological units. These data, along with Figure 11, indicate a BOD reduction of approximately 90 percent in the biological units. Coupled with the reduction in the primary clarifier, an overall reduction of better than 90 percent is indicated.

It is important to note that the first two lines of Table 12 represent the removal prior to the addition of supplemental phosphorus to the system. After phosphorus addition at BOD/P ratio of 100/1 was started, the removal efficiency was improved significantly.

The activated sludge settled well with concentration factors in the range of 3.5 to 6. A test also was run on the kinetics of the COD removal process (Figure 11).

TABLE 12 - COMPARISON OF COD AND BOD VALUES

Sample Description	No.	COD (mg/l)	BOD (mg/l)	Ratio of BOD to COD
Effluent from continuous-flow act. sludge. (Alum composite with dye)	1	407	125	0.31
	2	400	140	0.35
	3	675	110	0.16
Effluent from batch treatment unit. (Alum composite with dye)	1	740	77	0.10
	2	340	56	0.16
	3	540	35	0.06
	4	414	48	0.12
Effluent from batch treatment unit. (Alum composite without dye)	1	440	13	0.030
	2	545	16	0.029
	3	510	23	0.045
	4	246	17	0.068
	5	655	27	0.041
Alum process composite waste after primary treatment	1	1,485	1,010	0.68
	2	1,240	760	0.61
	3	1,310	780	0.60
	4	1,470	800	0.54

All COD removal which occurs takes place with 10 to 15 hr. This agrees with the results of the oxygen uptake curves plotted in Figure 9, even though the sources of activated sludge were different.

The BOD exerted for a 14-day period by the pretreated alum process composite (with dye) and of the effluent from the continuous flow system is presented in Figure 12. For comparative purposes, BOD on the pre-treated samples was determined using settled wastewater and the settled effluent from the biological unit as seed. There was no significant difference in the rate of oxygen utilization nor in the total oxygen required for stabilization.

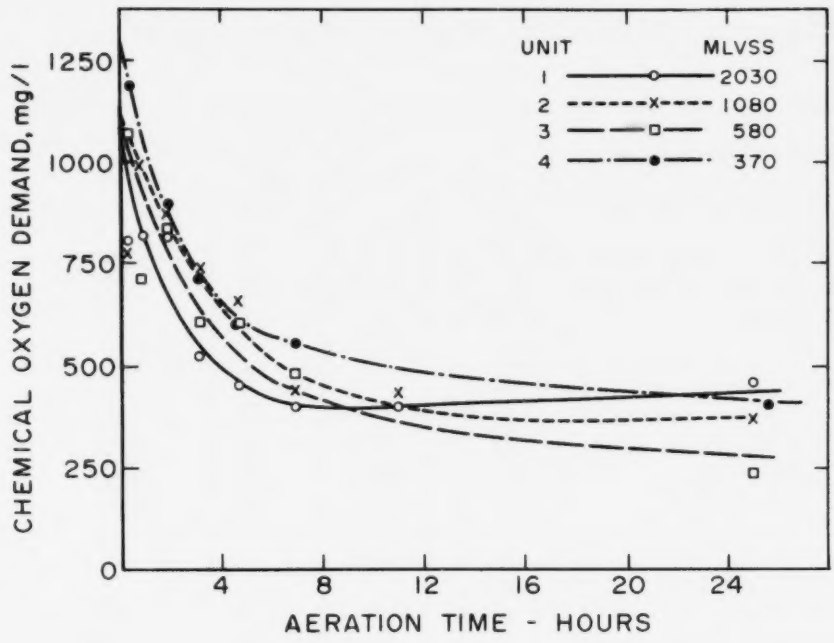

FIGURE 11 - COD REMAINING AS A FUNCTION OF AERATION TIME

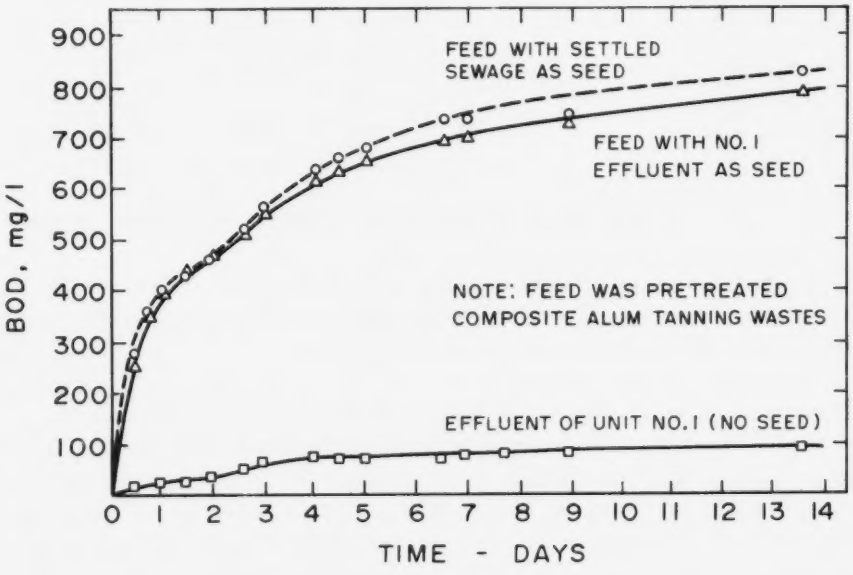

FIGURE 12 - BOD OF INFLUENT AND EFFLUENT OF CONTINUOUS FLOW SYSTEM

Oxygen Requirements of Biological Unit

The oxygen uptake of the mixed liquor in the activated sludge units was measured using a dissolved oxygen meter. During the short period of observation the air supply and waste feed to the unit were turned off. The MLVSS was 2,300 mg/l and the loading rate was 0.56 lb COD/day/lb of MLVSS.

Based on the data from these observations, the dissolved oxygen requirement for the activated sludge unit was found to be approximately 17 mg/l-hr, or 7.4 mg/l-hr-1,000 mg/l of MLVSS. This is essentially the same as the value of 7.5 commonly used for the terminal section of activated sludge units. A completely mixed system is comparable in loading to the terminus of a conventional system, since the COD of the effluent is equal to the COD at any point in a completely mixed system. Similar tests were made on the other continuously operating aeration unit, and essentially the same dissolved oxygen requirements were observed.

PROPOSED WASTE TREATMENT SYSTEM

Based on the results of the laboratory studies, it was concluded that the tannery wastes could be treated effectively, after equalization, by the standard operations of coagulation, sedimentation, and activated sludge-type biological treatment. It was recommended that a completely mixed activated sludge system be installed. No problems with toxicity were anticipated, and use of a completely mixed system with provision for flow equalization prior to the biological system was believed to be adequate to eliminate problems caused by the shock loads so common to tanneries.

The laboratory studies also showed that the common practice of combining all waste flows from tanneries prior to treatment is unwise. Certain waste streams, such as waste chrome tanning liquor and waste vegetable tanning liquor have different characteristics which make them more amenable to separate treatment. It was recommended that these waste streams be separated and given special treatment prior to introduction to the equalization basin.

The overall treatment scheme recommended for the Caldwell Lace Leather Company is shown in Figure 13. It is believed that this system can be used, with appropriate local modifications, to treat the waste from most tanneries for discharge to a receiving stream or to a municipal treatment plant. For tanneries not practicing all three types of tanning, the appropriate treament process(es) can be omitted.

Preceding page blank

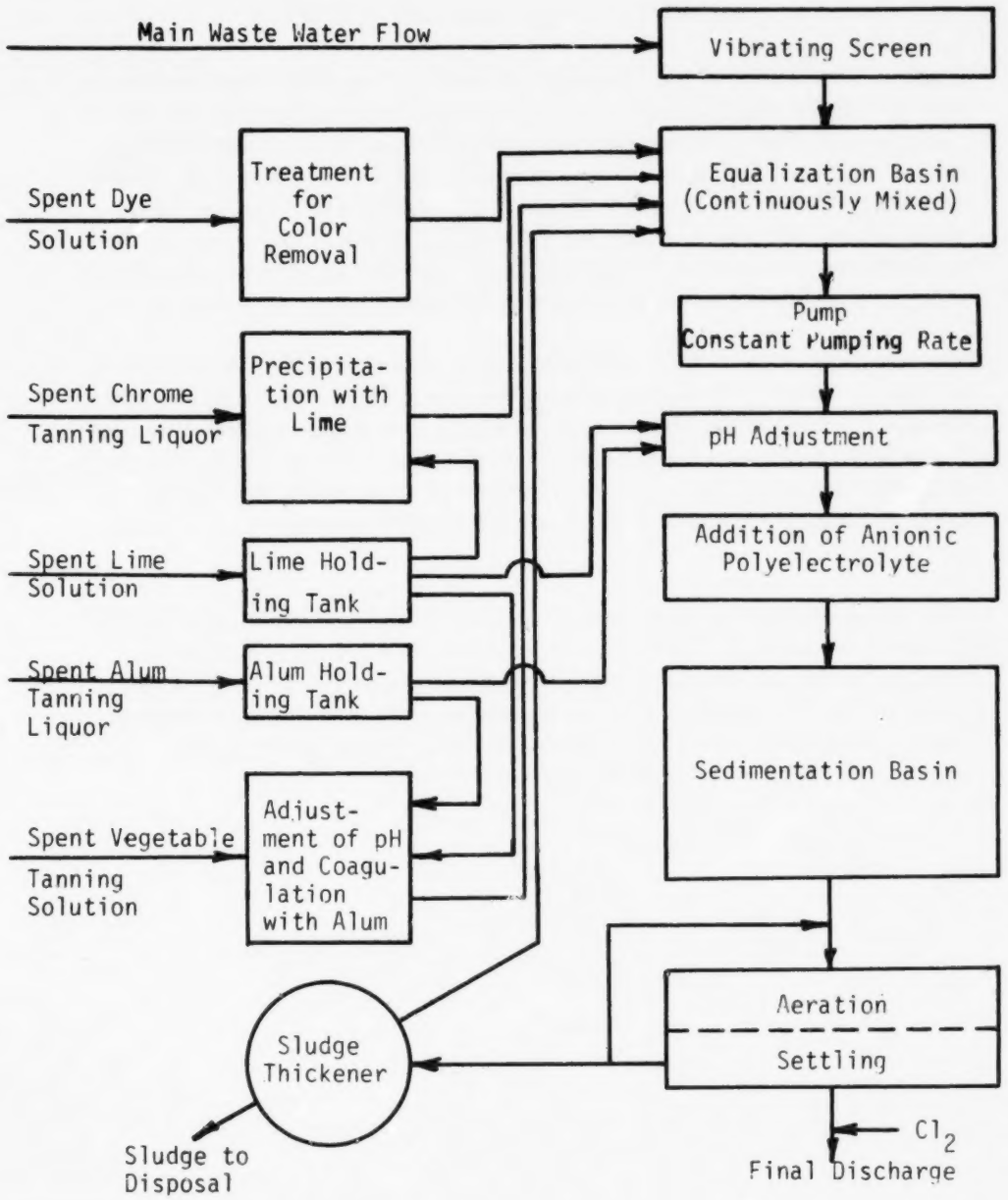

FIGURE 13 - OVERALL TREATMENT SCHEME PROPOSED FOR THE CALDWELL LACE LEATHER COMPANY

PROCESS DESIGN RECOMMENDATIONS

In the report of the laboratory studies (1), the following recommendations were made as to the process design of the biological system. Based on the results plotted in Figure 10, a maximum loading rate of 0.7 pounds of COD per day per pound of MLVSS was recommended. This is safely below the rate at which the efficiency of removal begins to be a function of loading rate. Based on a value of 65 percent for the BOD/COD ratio (Table 12), this corresponds to a loading rate of 0.45 on a BOD basis. This was considered to be a reasonable value for completely mixed systems.

Based on the data from Table 4, the total COD load from the process units is 2333 pounds per week. The load from the total plant might be as great as 3000 pounds per week. Assuming a conservative figure of 50 percent removal of COD in the primary sedimentation tank, the load on the biological system is 1500 pounds per week, or 300 pounds per day based on a five-day week. This would require 425 pounds of biological solids in the aeration unit.

The air required by the biological unit could be supplied by either diffused air or mechanical surface aerators. The oxygen requirements for 425 pounds of biological solids would be 122 pounds per day based on a conservative figure of 12 mg/l-hr-gram of biological solids.

The volume of excess sludge from the aeration unit was estimated to be 1000 gallons per day, based on 55 percent synthesis, an endogenous destruction rate of 5 percent per day and a solids concentration of 10,000 mg/l. Provision must be made for the disposal of this sludge, along with the solids from the primary clarifier. The volume to be handled could be considerably reduced by a gravity thickener.

Sufficient return sludge capacity should be provided to assure maintenance of an adequate solids level in the aeration unit. For a concentration factor of 3, a return sludge rate of 50 percent would be necessary. The pumping rate should be adjustable over a wide range to accomodate variations in the process.

It was predicted that the effluent from the proposed plant should have a 5-day BOD of 25 to 75 mg/l, a COD of 400 to 600 mg/l, and a suspended solids content of 25 to 100 mg/l. It was also stated that, in normal operation, the BOD of the effluent should be closer to 25 than 75 mg/l, while

the suspended solids content of the effluent would depend primarily on the efficiency of removal of micro-organisms in the secondary clarifier following the activated sludge unit. This is a function of several design variables, primarily inlet and outlet conditions, and the quality of the sludge in the process, which can be controlled by proper operation.

TREATMENT PLANT DESIGN

The tannery waste treatment plant was designed by Howard K. Bell, Consulting Engineers, Inc., of Lexington, Kentucky. The following description of the waste treatment plant is based largely on the engineering report submitted by the firm to the Kentucky Department of Health in June of 1968.

General Description of Waste Treatment Plant

The main waste flow is collected in the present wet well from which point it is pumped to the screen and equalization basin utilizing the old pump and a new one of the same capacity.

From the equalization basin the waste is pumped to a primary clarifier from which it flows by gravity through the aeration basin and final clarifier and thence to the receiving stream. A solution containing an anionic polymer can be added to the suction side of the pump delivering the waste to the primary tank.

Sludge is collected in the hopper of the primary clarifier and will be pumped to the sludge storage tank.

Aeration of the mixed liquor is provided by a mechanical aerator.

The settled activated sludge is returned from the final clarifier to the aeration basin by continuous pumping. Sludge is wasted as necessary by pumping sludge to the sludge holding tank or to the primary tank for settling with the primary sludge.

Chlorination facilities have not been installed at this time, but a chlorine contact basin and chlorination equipment can be installed at a later date if it is found to be necessary.

A lime solution holding tank was provided to store the lime solution pumped from the vats on a schedule of two days one week and three days the following week. The lime solution is allowed to drain from the holding tank into the raw waste wet well over the time period between fillings instead of slugging the equalization tank when the lime pits are emptied.

Sludge from the sludge thickening tank is hauled by tank truck to a land fill on a farm of the plant owner. Equipment is provided for covering the sludge in the fill as needed.

In view of the high ground water condition at the site and the resulting high expense for dewatering extensive excavations and the expense of protecting structures in the ground against uplift, steel basins and tanks located above ground level were used.

Detailed Description of Plant Treatment Units and Design Criteria

Chrome Tanning Solution - The chrome tanning solution is discharged in batches of about 200 gallons each at intervals of three times per week. A tank of 250 gallons capacity would have been sufficient to batch treat this waste but, in order for it to also be used for treating the vegetable tan liquor, a capacity of 450 gallons was provided. This tank is of wood stave construction and is located adjacent to the old alum solution tank.

Chrome waste is pumped to this tank from the tanning wheels with a portable pump. Hydrated lime is added in the amount of about six pounds to 200 gallons of waste to adjust the pH of the solution to 11.0 to 11.5 for precipitation of the chrome. Mixing of the lime into the solution is accomplished with a wooden paddle.

Vegetable Tanning Liquor - At the time the laboratory studies were made the plant was discharging about 200 gallons per day of spent vegetable tanning liquor. Since that time some of the vegetable tanning production has been transferred to another tannery and only 200 gallons per week is now being discharged to the waste stream.

Batch treatment of the vegetable tanning solution by mixing it with equal volumes of waste alum tanning solution was recommended by the laboratory studies report. However, since the vegetable tanning production was reduced to the point where only 200 gallons per week of tanning liquor is wasted, it did not appear that any pretreatment of this waste is necessary. A dilution ratio of about 800 to 1 is provided in the total waste flow and this dilution has resulted in no discernable increase in color in the total stream.

Spent Dye Solutions - Attempts to fortify and reuse dye solutions were recommended by the Vanderbilt report, and efforts in this direction were made by the tannery in order to decrease the amount of dye waste in the total stream flow. Eventually, they were able to achieve this, and each batch is now being used two or three times. This has resulted in a significant reduction in the dye waste flow and in the color of the mixed waste.

For 90 percent color removal from 800 gallons of dye waste per day, 27 pounds of carbon would have been required, and for 70 percent removal, 22 pounds would have been required. At a carbon cost of 26 cents per pound, the resulting daily costs would be $7.03 and $5.72 per day, respectively. This would have resulted in a monthly operation cost of approximately $150.

Because of the difficulty of determining the final quantity or the precise effect of the dye waste on the treated final effluent, an agreement was reached with the state pollution control authorities whereby color removal facilities would not be initially installed so long as they can be added later if found to be necessary. This has not been found necessary.

Screening and Equalization - Screening of the waste is mandatory to remove hair, flesh particles, and bits of leather from the waste stream. Preliminary studies were conducted using a vibrating screen, but during construction, a sloping slotted screen was substituted. This type of screen had just appeared on the market and was especially recommended for applications such as this.

Equalization Basin - Because of the variations in waste flow and characteristics and the necessity of operating the biological process on weekends when the plant is not in operation, some type of equalization basin was necessary.

For an average weekly flow of approximately 160,000 gallons it was proposed to feed the waste to the treatment plant as follows:

Weekdays - 1500 gallons per hour from 7 am to 5 pm
750 gallons per hour from 5 pm to 7 am

Weekends - 750 gallons per hour

This pumping schedule results in a daily design flow of 25,500 gallons per day for weekdays and a weekly flow of 163,500 gallons. Design of sedimentation basins and other facilities with short detention times was based on the daytime flowrate of 1500 gallons per hour or 25 gallons per minute. The average weekday flowrate of 25,500 gallons per day is 17.7 gallons per minute.

If an equalization basin of 50,000 gallons or less had been constructed, it would have been necessary to schedule the pumping rates to the treatment units so that the basin was essentially empty on Monday morning. This would have resulted in unequalized, undiluted waste being pumped directly to the treatment units on Monday morning. To prevent this, a basin of 62,500 gallons capacity was provided so that a buffer volume of 12,000 to 15,000 gallons of waste remains in the tank at the start of operations on Monday morning.

A 10-hp mechanical mixer is mounted on beams above the tank, and has turbine blades located near the bottom of the tank. An air compressor provides about 10 cfm of air, released below the turbine blades, to prevent anaerobic conditions.

Primary Clarifier - A surface loading of 635 gallons per day per square foot and a detention of 1.5 hours was provided for the primary clarifier at the design flow of 1500 gallons per hour. A conical hopper bottom with a 60-degree slope provides for storage and some compaction of sludge. A chamber was provided on the outside of the tank to provide a two-minute reaction time with the coagulant aid prior to entering the settling basin.

Aeration Basin - The report recommended a loading of about 0.70 pounds COD per day per pound of mixed liquor volatile suspended solids. A basin with capacity of one day's average flow of 25,500 gallons was provided.

The design load is 3,000 pounds of COD per week, and 50% of this load was assumed to be removed in the primary clarifier, thus leaving 1,500 pounds of COD to reach the biological process. At the proposed treatment rates the plant will handle 25,500 gallons per day for five days, or a daily flow of 15.6% of the weekly flow. Thus, the design daily COD load to the biological process was 234 pounds and the maximum day of 36,000 gallons would provide 330 pounds of COD.

The design for the maximum day COD required 330/.70 = 472 pounds of MLVSS. At the average day flow, the loading would be 0.50 pounds of COD per day per pound of MLVSS. In a basin of 25,500 gallons capacity this would result in a MLVSS concentration of 2,220 mg/l and a total MLSS concentration of 3,470 mg/l, which is the approximate concentration at which the pilot tests were run.

Oxygenation is provided by a 5-hp mechanical surface aerator. Calculations indicated that a 3-hp unit would have been sufficient, but a 5-hp unit was provided to give a slight margin of safety.

Final Clarifier - A circular center-feed clarifier with a 45-degree conical bottom was provided following the aeration basin. The surface loading at the design flow of 1500 gallons per hour is 653 gal/day-sq ft, and the detention time is two hours. Settled sludge is pumped continuously from the point of the cone.

Sludge Concentration and Storage Tank - The laboratory data showed that after one hour of settling the sludge volume is about 25 percent of the original and that after 14 hours of settling the volume of sludge is reduced to about one-half of the one-hour volume. On the basis of 25,500 gallons flow per day, this would result in a 3,190 gallons of primary sludge per day. Waste activated sludge was projected at about 1,000 gallons per day at 1 percent solids concentration. Thus, the expected solids volume was 4,190 gallons per day. A circular tank with a conical bottom was constructed to provide 12,570 gallons of sludge storage, or about three days production.

This capacity was considered to be conservative, since this sludge volume was based on the total flow from the plant, whereas the sludge volume measurements were made on the composite alum tanning process waste alone. Additional storage time in the sludge storage basin was expected to result in an increase in the solids concentration and, thus, in a lesser quantity of sludge to be hauled away.

Piping was provided from the sludge storage tank to the suction of the raw waste pumps and an alternate pump discharge line was provided for filling the tank truck.

Lime Waste Storage - Lime waste is discharged from the beam house vats every other work day, making four days one week and three days the next week. The volume of the solution added to the vats is approximately 2,200 gallons. It is desirable to distribute this flow somewhat evenly into the equalization basin, so a new 2500-gallon storage tank for this purpose was provided.

Nutrient Requirements - The laboratory studies found that the industrial waste does not contain sufficient phosphorus to support the biological life in the system. The phosphorus required is one pound per 100 pounds of BOD applied to the secondary system. The average weekly BOD load is 916 pounds, so 9.16 pounds of phosphorus per week would be required.

The most economical source of phosphorus is Triple Super Phosphate fertilizer which contains 42 percent P_2O_5 and costs approximately $5.00 per 100 pounds. About 50 pounds of Triple Super Phosphate is required per week so, ten pounds of the fertilizer was originally added to the qualization basin each working day of the week.

Laboratory Building - A small prefabricated steel building housing a laboratory, the pumps, electrical gear, air compressor, polyelectrolyte dissolving tank and feeder, and pH recorder was provided adjacent to the waste treatment plant.

CONSTRUCTION AND STARTUP

The waste treatment plant was constructed, essentially as described in the preliminary report, during 1970. Considerable delay was experienced in beginning construction because of the difficulty of securing an experienced contractor to build a small plant in a small town. Further delay was experienced later in the construction phase because of faulty instructions which accompanied the paint selected for the interior of the treatment unit tanks. Because of some omitted steps in the instructions, the paint all peeled off when the tanks were filled. This difficulty too was rectified and construction was finally completed in June, 1970.

Initially, attempts were made to start the biological process without resorting to seeding with sludge from another plant, but these attempts were unsuccessful. Sufficient biological growth would not take place. Eventually, two tank trucks of activated sludge from a nearby plant were added to the aerator, and the plant began functioning. The reasons for the lack of spontaneous biological growth were not determined, but possibilities include the extremely high salt content of the waste, the presence of inhibiting substances, or the presence of a heavy foam blanket.

Foaming has been an operational problem at the plant from the beginning. Foaming occurs both in the equalization basin and in the aerator. Antifoaming agents currently keep the problem under control, but the cost has led the tannery to also consider the use of sprays using final effluent to knock down the foam in the basins. The source of the foam is probably the detergents used in the tanning process.

The initial performance of the plant could be described as fair. Many problems were caused by lack of a trained operator and by continued problems with the pumps. It is an accepted fact that it is difficult to find reliable heavy-duty pumps in small sizes, and this fact has been confirmed again in this case. In addition, the organic load on the treatment plant was significantly higher than expected. The BOD of the influent averaged 2500 mg/l, almost double the value of 1300 mg/l found during the laboratory studies.

Initially, the effluent BOD, predicted by the laboratory study report to be in the range of 25 to 75 mg/l, varied between 50 and 200 mg/l. Then, in the November, 1970, to February, 1971, period, it rose to over 300 mg/l, obviously much too high. However, most of the effluent BOD was caused by carryover of suspended solids from the final clarifier.

The loss of suspended solids was caused by several factors, but primarily by a MLSS concentration in the aerator which was too high, and by unstable operation of the pumps. Unstable pump operation led to many hydraulic surges, which stirred up the ligh flocculent solids in the final clarifier. Also, the return sludge line frequently clogged, either partially or completely, and the sludge layer in the clarifier built up to the level of the bottom of the skirt around the center influent well. The water flowing out through the narrow space between the bottom of the skirt and the sludge layer was therefore increased in velocity and scoured up considerable sludge which rose to the surface where it was swept over the weir. The MLSS concentration, originally planned for the level of 3000-3500 mg/l, averaged over 5000 mg/l. This increased the solids loading on the clarifier, creating density currents and contributing to the problem of rising clouds of sludge and the resulting solids loss. The effluent suspended solids averaged between 300 and 600 mg/l, and values as high as 1200 mg/l were obtained.

By March, 1971, a capable operator had been secured and partially trained, and the author had visited the plant as a consultant and identified some of the reasons for the plant's poor performance. The MLSS in the aerator was lowered from 13,400 mg/l to the range of 4000-5000 mg/l, and the effluent suspended solids dropped to the range of 50-150 mg/l.

Further improvement in average plant performance occurred during the summer of 1971. Arrangements were made with the Environmental Protection Agency, through its Office of Operations, Radiological and Industrial Waste Evaluation Section, in Cincinnati, Ohio, to perform an industrial waste survey of the tannery's waste treatment system. The objective of the survey was to collect comprehensive data from which the efficiency of the treatment system could be evaluated. The evaluation of the performance of the plant was necessary to confirm or refute the findings of the laboratory studies and complete this final report of the project. A secondary objective of the study was to obtain data to aid in the establishment of effluent guidelines for the tannery industry.

EVALUATION OF PLANT PERFORMANCE

The industrial waste survey was conducted by EPA personnel during the period October 28, 1971, through November 10, 1971. During the 14-day survey, 24-hour composite samples (beginning at 8:00 a.m.) were collected of the primary clarifier influent, the primary clarifier effluent, and the final effluent. On several occasions, the automatic samplers failed, and grab samples were taken as substitutes. Additional grab samples were collected from the aerator, the sludge recirculation stream, and the final effluent for determination of suspended solids, pH, sulfides, nitrites, dissolved oxygen (DO), and sludge volume index (SVI).

All analyses, except where specifically mentioned, were conducted in accordance with "standard methods." Total organic carbon (TOC) was determined with a Beckman Carbon Analyzer. Dissolved Oxygen was determined with a Weston and Stack oxygen analyzer. Atomic absorption methods were used for analyses of iron, total chromium, and aluminum. Flow rates were determined by "spill and fill" methods.

Water Flow

The flow through the treatment plant during the survey is in question. Records were kept of both plant water use (from the plant water meter) and of waste flow. The two groups of data do not agree. The apparent waste flow averaged 11.5 gpm during the survey, while the apparent average plant water use was 14.5 gpm. It has been assumed during the entire project that the waste flow would be approximately the same as the plant water use. Some small loss is expected, but not the apparent loss of 3.0 gpm, or 21 percent. It is not known which, if either, group of data is in error, or if some other factor caused the two records of flow to be so different.

The flow data obtained during the survey are shown in Table 13. The presence of the equalization tank means that the daily values of flow will not agree. The waste flow will be more constant than the water use. However, the totals and averages over the two-week period should agree closely.

The water use during the survey was less than that found during the laboratory study three-and-a-half years earlier. The average weekday flow of 26,860 gal/day compares with the value of 32,000 found earlier, and the weekly flow of 145,500 gal/week compares with the value of 160,000 gal/week found earlier.

TABLE 13 - WATER FLOW DURING SURVEY

Date	Day	Water Use		Waste Flow	
		(gal/day)	(gal/min)	(gal/day)	(gal/min)
Oct. 28	Thur.	31,850	22.1	18,400	12.8
Oct. 29	Fri.	27,365	19.0	21,000	14.6
Oct. 30	Sat.	15,265	5.3	21,000	14.6
Oct. 31	Sun.			10,100	7.0
Nov. 1	Mon.	23,040	16.0	19,450	13.5
Nov. 2	Tues.	26,995	18.8	17,700	12.3
Nov. 3	Wed.	30,455	21.2	12,250	8.5
Nov. 4	Thur.	28,590	19.8	11,250	7.8
Nov. 5	Fri.	26,865	18.7	18,000	12.5
Nov. 6	Sat.	7,405	2.6	14,000	9.7
Nov. 7	Sun.			--	-
Nov. 8	Mon.	10,245	7.1	19,700	13.7
Nov. 9	Tues.	35,055	24.4	20,000	13.9
Nov. 10	Wed.	28,180	19.5	12,950	9.0
TOTAL		291,310		215,800+	
AVE.		20,800	14.5	16,600	11.5
AVE WEEKDAY		26,860	18.7	17,100	11.9

The average flowrate of waste through the treatment plant during a period must be known in order to calculate the loading of various waste constituents on the plant or on the stream. For this report, the values of flow used to calculate loading were those reported by the survey team for waste flow, not water use. Since the waste flow will not match the variation of water use with time because of the equalization basin, the water use records could not be used even if it were certain that they were accurate.

Summary of Plant Performance

The overall performance of the waste treatment plant during the EPA survey is tabulated in Table 14. An overall assessment of the performance, simply stated, could be that efficiency is good, but that there are still several areas that need further investigation and improvement. The principle area

TABLE 14 - MEAN VALUES OF PARAMETERS DURING EPA SURVEY

Parameter \ Sample Location	Primary Influent	Primary Effluent	Secondary Effluent
BOD_5, mg/l	1437	619	96
COD_T, mg/l	4016	1149	481
COD_F, mg/l	987	975	254
TOC_T, mg/l	1191	388	150
TOC_F, mg/l	354	356	76
TKN, mg/l	490	-	322
Org. N, mg/l	328	-	175
NH_3-N, mg/l	162	-	147
NO_2-N, mg/l	0.1	-	34*
NO_3-N, mg/l	0.1	-	0.4
SS, mg/l	3135	110	223
pH, units	7.6	7.5	7.3
Temp., °F	-	-	56.8
Sulfide, mg/l	7.9	8.6	0
Alkalinity, mg/l	516	-	141
Acidity, mg/l	181	-	46.5
Sulfates, mg/l	2743	-	3071
Chlorides, mg/l	5174	-	5127
Phosphorus, mg/l	22.8	-	13.4
DO, mg/l**	-	-	5.7
TDS, mg/l	12,795	13,242	13,016

*Mean value of grab samples only
**Mean value of readings from DO probe only

of concern is solids carryover in the secondary clarifier, leading to high BOD_5 in the final effluent. Specific variables will be discussed in more detail later in this section.

TABLE 15 - BOD LOAD DURING SURVEY

Date		Flow (gal/day)	BOD to Primary		BOD to Secondary		BOD to Stream	
			(mg/l)	($\frac{lb}{day}$)	(mg/l)	($\frac{lb}{day}$)	(mg/l)	($\frac{lb}{day}$)
Thur	Oct 28	18,400	1567	240	540	83	39	6
Fri	29	21,000	1450	254	670	107	37	6
Sat	30	21,000	2133	374	960	168	D	-
Sun	31	10,100	1250	105	800	67	D	-
Mon	Nov 1	19,450	1400	227	590	96	D	-
Tues	2	17,700	2100	309	700	103	D	-
Wed	3	12,250	1533	160	590	62	D	-
Thur	4	11,250	1583	148	530	50	D	-
Fri	5	18,000	1650	248	740	111	144	22
Sat	6	14,000	1166	136	470	55	115	13
Sun	7	--	--	--	--	--	127	-
Mon	8	19,700	850	139	420	69	180	30
Tues	9	20,000	883	147	540	90	82	14
Wed	10	12,950	1117	121	500	54	45	5
	Average	16,600	1437	199	619	86	96	14
	Design	25,500	1320	280	660	140	50	10

D = Dissolved Oxygen Depleted

BOD and COD Load

Tables 15 and 16 present the daily average values of BOD and COD, respectively, which were measured during the survey. The average values and the values used for design purposes are also presented, and all concentration values are converted to pounds per day, using the measured daily average waste flow.

The BOD concentrations in the raw waste and in the primary effluent, 1437 mg/l and 619 mg/l, are close to those assumed for design, 1320 mg/l and 660 mg/l, but the actual effluent BOD was higher, 96 mg/l vs. 50 mg/l. The measured load to both the primary and secondary systems is less than

TABLE 16 - COD LOAD DURING SURVEY

Date	Flow (gal/day)	COD to Primary		COD to Secondary		COD to Stream	
		(mg/l)	($\frac{lb}{day}$)	(mg/l)	($\frac{lb}{day}$)	(mg/l)	($\frac{lb}{day}$)
Oct 28	18,400	5670	870	1200	184	315	48
29	21,000	3810	666	1280	224	291	51
30	21,000	3860	675	1310	229	716	125
31	10, 000	3110	262	1160	98	428	36
1	19,450	4080	662	1060	172	413	67
2	17,700	6000	885	1340	198	673	99
3	12,250	4080	416	1180	120	661	68
4	11,250	3840	360	1070	100	553	52
5	18,000	3840	576	1090	164	453	68
6	14,000	4140	482	1030	120	532	62
7	--	--	--	--	--	480	-
8	19,700	3250	533	1390	228	629	103
9	20,000	2500	416	950	158	442	74
10	12,950	4030	435	874	94	154	17
Average	16,600	4016	575	1149	159	481	66
Design	25,500	2200	468	1100	234	500	106

that assumed for design, however, because of the lower flow. The BOD removal efficiency of the primary clarifier was 57%, compared to an assumed 50%; the efficiency of the secondary system was 84.5%, compared to an assumed 92%; and the overall efficiency was 93%, compared to the assumed 96%. The failure of the plant to achieve the design efficiency was primarily due to excess solids carryover from the secondary clarifier, as will be shown later.

The COD concentration in the raw waste was almost double the assumed value of 2200 mg/l, but the measured concentrations in the primary and secondary effluents were very close to the assumed values of 1100 mg/l and 500 mg/l. The COD load on the primary system was only slightly higher

TABLE 17 - BOD LOADING RATES DURING SURVEY

Date	BOD (lb/day)	MLSS (mg/l)	MLVSS (mg/l)	MLSS Loading (1/day)	MLVSS Loading (1/day)
Oct 28	83	3584	2108	0.09	0.15
29	107	3380	2536	0.12	0.16
30	168	--	--	--	--
31	67	--	--	--	--
Nov 1	96	3528	--	0.10	--
2	103	3585	--	0.11	--
3	62	3813	--	0.06	--
4	50	3352	--	0.06	--
5	111	3476	--	0.12	--
6	55	--	--	--	--
7	--	--	--	--	--
8	69	3638	2624	0.07	0.10
9	90	4263	--	0.08	--
10	54	4145	2860	0.05	0.07
Average	86	3676	2532	0.09	0.13
Design	140	3470	2220	0.15	0.24

than that assumed for design, however, because of the lower flow, and the COD load in the secondary influent and effluent were significantly less than the assumed values, because of the reduced flow and the increased efficiency of the primary clarifier. The actual efficiency of 71% is significantly greater than the 50% assumed for design. The COD removal efficiency found during laboratory studies was 67%, but a value of only 50% was assumed for design to allow for the normal reduction in efficiency due to turbulence and density currents not present in the laboratory column. The COD reduction in the secondary system was 58%, compared to the assumed 55%, and the overall efficiency was 88%, compared to the assumed efficiency of 77%.

TABLE 18 - COD LOADING RATES DURING SURVEY

Date	COD (lb/day)	MLSS (mg/l)	MLVSS (mg/l)	MLSS Loading (1/day)	MLVSS Loading (1/day)
Oct. 28	184	3584	2108	0.20	0.32
29	224	3380	2536	0.25	0.34
30	229	--	--	--	--
31	98	--	--	--	--
Nov. 1	172	3528	--	0.19	--
2	198	3585	--	0.21	--
3	120	3813	--	0.12	--
4	100	3352	--	0.11	--
5	164	3476	--	0.18	--
6	120	--	--	--	--
7	--	--	--	--	--
8	228	3638	2624	0.24	0.34
9	158	4263	--	0.15	--
10	94	4145	2860	0.09	0.13
Average	159	3676	2532	0.17	0.24
Design	234	3470	2220	0.26	0.39

The BOD and COD loading rates during the survey, based on both MLSS and MLVSS, are presented in Tables 17 and 18. The values of MLSS are taken both from the EPA survey and from plant records. Most of the EPA survey records were rejected as being much too low because of an inappropriate sampler. When grab samples were used, the EPA survey results and the plant records agreed closely, and an average value was used.

Values of MLVSS were only from the EPA survey results. Values which were obtained using inappropriate sampling methods were not used. The

inappropriate sampler consisted of a cup which was lowered periodically on a timed signal into a perforated pipe extending down into the aeration basin. However, values obtained using this sampler were only about 60% of those obtained when grab samples were analyzed. The perforated pipe created a semi-quiescent environment inside the pipe and the lack of turbulence caused the sludge to settle somewhat. The sludge concentration was thus lower inside the pipe, especially near the surface where the sample cup was primarily filled, than the sludge concentration outside the pipe. The cup sampler was discarded on November 7, when the discrepancy in concentrations using the two sampling methods was discovered.

In calculating the loading rates, the estimated solids in the secondary clarifier were added to the solids in the aerator to obtain the total solids in the system. The clarifier was assumed to contain solids at a concentration of 15,000 mg/l to a level two feet above the conical section. This produced a total solids content of 175 lb in the clarifier and volatile solids content of 120 lb. Under normal operating conditions, with the return sludge pumps working well and the sludge lines clear, the solids content of the clarifier would be much less than this.

The BOD loading rate found during the EPA survey was only about 60% of the design loading rate, both because of the lower BOD load and the slightly higher solids concentrations. The BOD loading, based on volatile solids, was only 0.13/day, compared to the design value of 0.24. (The design value would be 0.30/day if the solids content of the clarifier were ignored, and the average survey value would be 0.16/day.) The value of 0.13/day places the plant in the category of an extended aeration plant, whereas a standard loading was assumed.

The laboratory study report recommended a COD loading rate of 0.70/day, based on volatile solids. The design report adopted a COD loading rate of 0.70/day for the maximum day's flow of 36,000 gal, equivalent to a loading rate of 0.50/day for the normal day's flow of 25,500 gal. This rate becomes 0.39/day when the approximately 120 lb of volatile solids in the clarifier during the study is considered. The actual average COD loading rate found during the EPA survey was only 0.24/day, about one-half the intended design value.

The BOD/COD ratio found during the laboratory study was 0.60. The average BOD/COD ratio for the primary effluent found during the EPA

survey was 0.54. The ratio found for the raw waste was only 0.36. Thus, much of the increase in the raw waste COD from the values found during the earlier survey consisted of non-biodegradable material which was removed by the primary clarifier.

The results of the EPA survey show that the treatment plant was definitely underloaded during the survey. Based on these results, the MLSS in the aerator should probably be lowered to the range of 2500 mg/l in order to reduce the solids load on the secondary clarifier and, hopefully, reduce the solids carryover. If this were done, and the volatile solids content of the clarifier could be kept to 50 lb, the COD loading rate would still be only 0.38/day and the BOD loading rate only 0.21/day if the load did not increase, well within safe limits.

Organic Matter Removal

The performance of the treatment plant in removing organic material during the EPA survey was generally good. The organic content of the waste was measured in terms of BOD_5, COD, and TOC during the survey, with the COD and TOC tests run on both total and filtered samples. The results, in terms of maximum, mean, and minimum, are presented in Table 19.

Table 19 contains no real surprises or anomalies. The results of the daily samples are relatively consistent, with the low values almost always occurting on November 8 or 9, as illustrated in Tables 14-17. As expected, there is less variation from day to day as the sampling point advances through the treatment plant.

The most striking result of the data in Table 18 is the difference in values between filtered and total COD and TOC of the final effluent. This result was expected because of the obvious loss of solids from the secondary clarifier. The data shows that the total COD and TOC is approximately double the filtered values. This result illustrates the importance of final clarifier performance in producing a good effluent, and the importance of improving performance in this particular case. In this case, where half the final effluent COD is due to solids loss, a reduction in effluent COD of approximately 30 to 40% should result if the efficiency of the final clarifier improved to the point where it could be considered average.

TABLE 19 - ORGANIC MATTER REMOVALS DURING EPA SURVEY

Parameter	Sample Location	Primary Influent	Primary Effluent	Secondary Effluent
BOD_5, mg/l	Maximum	2133	960	180
	Mean	1437	619	96
	Minimum	850	420	37
COD_T, mg/l	Maximum	6000	1390	716
	Mean	4016	1149	481
	Minimum	2500	874	154
COD_F, mg/l	Maximum	1250	1130	346
	Mean	987	975	254
	Minimum	787	768	139
TOC_T, mg/l	Maximum	2000	455	212
	Mean	1191	388	150
	Minimum	740	295	79
TOC_F, mg/l	Maximum	500	480	97
	Mean	354	356	76
	Minimum	260	295	62

Solids

The solids content of the waste is shown in Table 20. The high dissolved solids content (about 40% of that of seawater) results from the initial rinse to remove the salt used to preserve the hides. Although much higher than most wastes, the concentration does not appear to inhibit the biological system.

The data shows that the primary clarifier did an excellent job of removing suspended solids, with an average removal of slightly over 96%. Only a few high values prevented the average removal from being even greater. The median value of suspended solids in the primary effluent was 56 mg/l.

TABLE 20 - SUSPENDED SOLIDS DURING EPA SURVEY

Sample Parameter / Location	Raw Waste	Primary Effluent	Secondary Effluent
Dissolved Solids, mg/l			
Maximum	14,754	14,863	13,942
Mean	12,795	13,242	13,016
Minimum	9,451	11,134	12,251
Suspended Solids, mg/l			
Maximum		546	400
Mean	3,135	110	223
Minimum		12	56

The secondary clarifier, however, did not perform well at all, as already noted. The average effluent suspended solids of 223 mg/l is much too high, and should be about what the minimum actually was--56 mg/l.

TABLE 21 - MEAN VALUES OF NITROGEN FORMS DURING EPA SURVEY

Sample Parameter / Location	Primary Influent	Primary Effluent	Secondary Effluent
TKN, mg/l	435	308	274
Org.-N, mg/l	250	132	117
NH_3-N, mg/l	185	176	158
NO_2^--N, mg/l	0.1	0.1	31
NO_3^--N, mg/l	0.1	0.1	0.2

Nitrogen

The wastewater is high in nitrogen. There are three major sources of nitrogen, organic solids from the hides, dimethyl amine used in the lime soaking pits as an alternative to sodium sulfide, and ammonium sulfate used in the alum process. Table 21 contains the mean values of Total Kjeldahl Nitrogen (TKN), Organic Nitrogen, Ammonia Nitrogen (NH_3-N), Nitrate Nitrogen (NO_2^--N), and Nitrate Nitrogen ($NO_3^=$-N) in the primary influent, primary effluent, and secondary effluent for the last four days of the survey, which were the only days for which data is available from all three sampling locations.

The removal of TKN is only fair for a plant of this type - 37%. Examination of the data in Table 21 shows that 47% of the organic nitrogen is removed in the primary clarifier, but very little is removed in the secondary system. Of the 117 mg/l of organic nitrogen in the final effluent, approximately 15 mg/l can be attributed to the activated sludge solids carryover. Of the organic nitrogen "removed" by the primary clarifier, some undoubtedly was in the solid form and settled with the sludge, but some was probably also hydrolyzed to the ammonia form.

The ammonia nitrogen content of the waste decreased only 5% through the primary clarifier, but it must be kept in mind that both removal (via sedimentation) and addition (via conversion from the organic form) was probably taking place. However, since most of the ammonia nitrogen is expected to be in the dissolved form, little sedimentation was expected.

The amount of ammonia nitrogen removed in the secondary system is low, considering the low actual loading rate, but not lower than expected, since the planned loading rate did not provide for complete nitrification. Part of the removal of ammonia nitrogen can be attributed to stripping of the relatively volatile dimethyl amine and part to biological oxidation to nitrite.

The nitrification step is obviously being inhibited by some mechanism, since nitrite concentrations in the effluent are extremely high and nitrate concentrations almost negligible. Almost the entire 33-mg/l drop in TKN through the secondary system shows up as an accumulation of nitrite (31 mg/l). Even allowing for the fact that some of the TKN in the secondary effluent is essentially added by solids carryover rather than the residual of what entered the system, the low nitrate concentration shows that very little conversion of nitrite to nitrate took place. Usually this phenomenon is due to low oxygen

levels, but the oxygen content of the aerator during the survey averaged 8.5 mg/l, so this could not be the cause in this case. It is likely, in this case, that the problem can be attributed to some inhibiting substance, possibly a detergent used in the leather finishing process. It is also possible that the high nitrite buildup was partially responsible for the lack of greater conversion of ammonia to nitrite.

The nitrogen concentration of the effluent could be reduced indirectly by reducing the amount of dimethyl amine used in the soaking process, and returning to a greater use of sodium sulfide. The survey showed that the relatively low level of sulfides present in the waste was completely oxidized by the secondary system. However, there is no evidence at present that the nitrogen discharged to the stream significantly affects either the oxygen level or the productivity of the water. This is an area which would merit further investigation.

Water Temperature

The temperature of the aerator contents at the beginning of the survey was 70°F, but declined to the mid-forties by the end of the survey because of the onset of cold weather. The above-ground steel tanks and the long detention times makes the temperature of the aerator closely follow trends in average daily temperature. However, no significant effect of temperature on treatment efficiency can be noted--possibly because of the long detention times and low loading rate during the survey.

pH

The pH of the raw waste varies greatly, but the equalization basin is very effective in moderating extreme changes in pH. Discharges from the lime pits are pumped to a storage tank and bled into the equalization tank gradually. However, the acid alum tanning solutions and dyeing solutions are dumped directly.

Close attention by the production supervisor of the tannery and the waste treatment plant operator is necessary to monitor the pH of the equalization basin and pump lime solution from the storage tank into the equalization basin whenever a discharge of tanning or dyeing solution depresses the pH below 7.0. This attention was satisfactorily provided during the EPA survey by the regular plant operator. The daily average pH of the aeration basin

never varied outside the range of 6.7 to 7.7. When the lime solution storage is depleted, lime in 50-pound bags is used to raise the pH, if necessary.

Sulfides

The concentration of sulfide in the waste is not high, because much of the sodium sulfide formerly used in the lime soaking pits as an aid to unhairing has been replaced by dimethyl amine. The low concentration of about 8 mg/l is completely removed by the secondary system.

Phosphorus

During the laboratory studies, the waste was shown to be phosphorus deficient, so the design report recommended that triple superphosphate be added to the equalization tank as a nutrient. Later, the point of addition was moved directly to the aerator, since the high pH values sometimes experienced in the equalization basin were precipitating it as calcium and aluminum phosphates.

Values of phosphorus determined during the EPA survey showed the waste not to be phosphorus deficient. The average of 22.8 mg/l in the primary influent is almost four times the 6.2 mg/l needed for biological growth, assuming a 1:100 P:BOD ratio. Actually, less than that is probably needed because the currently low loading rate causes little net cell growth and much biological phosphorus is recycled. Thus, the average effluent concentration was a high 13.4 mg/l.

There are two known sources of phosphorus--the organic phosphorus in the organic waste from the hides, and sodium hexametaphosphate used in the vegetable tanning process. Some of the organic phosphorus was probably removed in the primary clarifier. How much is unknown, because phosphorus was not run on the primary effluent.

During the survey, the regular operator obtained a Hach kit for determination of phosphorus on the secondary influent and effluent, and now hopes to add triple superphosphate when the concentration drops too low.

Dissolved Oxygen

The accurate measurement of dissolved oxygen concentrations in the aeration basin and in the final effluent by the Winkler method proved to be impossible because of the high nitrite levels. Therefore, the Winkler method was discarded and a dissolved oxygen probe substituted about halfway through the

survey. Dissolved oxygen in the aeration basin averaged 8.5 mg/l, and DO in the final effluent averaged 5.7 mg/l, with a low of 2.2 mg/l and a high of 8.5 mg/l. Concentrations in both locations are easily satisfactory and show that the aerator is more than large enough for sufficient aeration.

Heavy Metals

Heavy metals measured in the primary influent and secondary effluent were calcium, total chromium, hexavalent chromium, iron, aluminum, sodium, and boron. The boron and hexavalent chromium concentrations were determined only one time, on a composite sample of all samples taken during the entire survey. The mean values of the concentrations determined are shown in Table 22. All metal concentrations were relatively consistent from sample to sample except influent total chromium, which varied from 1.3 mg/l to 13.5 mg/l, and effluent aluminum, which varied from 1.0 mg/l to 18.2 mg/l.

TABLE 22 - MEAN VALUES OF HEAVY METALS DURING EPA SURVEY

Metal	Primary Influent	Secondary Effluent
Calcium, mg/l	478	485
Total Chromium, mg/l	6.5	0.4
Hexavalent Chromium, mg/l	0.03	0.01
Iron, mg/l	13.3	<1.0
Aluminum, mg/l	298	8.3
Sodium, mg/l	3798	3851
Boron, mg/l	0.83	0.96

As expected, calcium, sodium, and boron were essentially unaffected by treatment. However, since the hydroxides (or other complex precipitates) of iron, aluminum, and trivalent chromium are relatively insoluble at pH 7.5 and above, it is assumed that the removal of the metals occurred, at least partially, by precipitation in the primary clarifier. This cannot be shown definitely, however, because heavy metals were not run on the primary effluent.

Coliform Bacteria

Only a few coliform bacteria tests were conducted, because the samples had to be iced and sent to the Cincinnati laboratory for analysis. The results, shown in Table 23, are highly variable, and averages would be meaningless. The data do show, however, that the great majority of coliform bacteria in the final effluent are of non-fecal origin. Given the fact that the municipal waste treatment plant discharges into the stream at the same location and that there is no use of the stream by humans for drinking purposes or recreation, chlorination of the effluent does not seem justified on the basis of the present data.

TABLE 23 - COLIFORM COUNTS DURING EPA SURVEY*

Location of Sample and Coliform Type	Date			
	9/23/71	10/3/71	10/7/71	11/12/71
Primary Influent				
Total	170,000	--	--	--
Fecal	73,000	11,000	6,000	5,000
Primary Effluent				
Total	--	--	--	16,300,000
Fecal	--	2,600	1,800	3,000
Secondary Effluent				
Total	590,000	--	--	8,600,000
Fecal	29,000	1,300	2,400	430

*All counts expressed as coliform bacteria per 100 ml.

TREATMENT PLANT OPERATION*

The success of treating this particular tannery waste is determined largely upon the conscientiousness and training of the operator. Fortunately, the operator at Caldwell has both qualities which resulted in acceptable treatment of Caldwell's wastewater. Nevertheless, problems were encountered with pump failure, lines plugging, and pH monitoring equipment. On one occasion (11/7-8), the transfer line from the equalization basin to the Moyno pump became clogged which resulted in dry operation of the Moyno pump. The dry operation coupled with grit resulted in stator disintegration and scoring of the rotor which contributed to no-flow conditions to the system for about 12 hours. A stand-by Moyno pump was put into operation after the clogged line was blown with air. The efficiency of treatment was not affected after the shut-down period. The fact that the soluble TOC on the following day (longer operation time) was not significantly different than the mean value for the study suggests that the remaining soluble organics in the final effluent were highly refractory substances. Relatively nonbiodegradable detergents probably contribute significantly to the refractory load to the stream. The detergents also presented an aerator foam problem severe enough to warrant the use of an antifoaming agent. Caldwell may well investigate the use of spray nozzles to minimize foam in the aerator, possibly using final effluent as a source of water.

Another problem area is the sludge recirculation pump and associated transfer lines. Oberdorfer pump flow rates ranged from zero when clogged to 6.1 gal/min after cleaning. These flow rates were measured by the "spill and fill method" as opposed to reading flow rates from manometer-orifice measuring devices installed by the consulting engineer. It was recommended that all orifice plates be removed from transfer lines in an effort to minimize clogging in the relatively small openings and use "spill and fill" techniques for daily measurement of flow.

---

*These comments on plant operation are taken verbatum from the EPA survey report written by Ed Berg.

PLANT PERFORMANCE SINCE EPA SURVEY

In the months since the EPA survey, tannery personnel have worked to increase the efficiency of the waste treatment system by taking actions both inside the tannery and at the waste treatment plant. On the basis of records kept by the tannery for submission to the Kentucky Water Pollution Control Commission, the results have been excellent. Table 24 summarizes the data gathered from January, 1972, through June, 1972.

TABLE 24 - PLANT PERFORMANCE IN 1972

Month	Water Flow (gal/day)	SS(mg/l)		%	BOD(mg/l)		%
		In	Out	Reduc.	In	Out	Reduc.
Jan	22,300	1406	55	96	510	39	92
Feb	23,300	1690	47	97	229	17	91
Mar	24,100	1358	66	95	201	19	90
Apr	22,300	2400	61	97	416	20	95
May	23,700	2098	34	97	666	27	96
June	24,000	3032	52	98	664	21	96
EPA Ave.	20,800	3135	223	93	1437	96	94

The effluent of the plant in 1972 is a marked improvement over that found during the EPA survey. This is due to two influences. First, the strength of the incoming waste is considerably lower in both SS and BOD. Secondly, the percentage removal of both SS and BOD has improved.

The final effluent SS content is almost totally a function of the efficiency of the secondary clarifier. During the EPA survey, it will be recalled that the secondary effluent had twice the SS content of the primary effluent. The much better performance of the secondary clarifier has reduced the SS loss to less than 25% of that during the EPA survey.

Preceding page blank

The reduction in SS loss also causes a reduction in final effluent BOD almost as great--to only 25% of that found during the EPA survey. The current performance of the waste treatment plant is equal to or better than the upper limits of performance estimated by the laboratory study and would be difficult to improve upon significantly.

The plant is loaded even lighter now than it was during the EPA survey, when it was definitely underloaded. The reduction in overall plant loading is not quite as great as the reduction in SS and BOD, because the flow, as measured by water use (7-day per week average of water meter reading) increased 15% over that during the EPA survey. True average loadings cannot be computed from available data because BOD and SS tests are not run every day and no tests are run on the primary effluent, but it is certain that the secondary system is operating in the extended aeration range. Mixed liquor suspended solids content of the aerator has averaged about 6000 mg/l during 1972, but sludge is withdrawn somewhat more regularly than before, so fluctuations are not as great.

Several reasons have been advanced by the tannery management for the drop in waste loading. There has been some small reduction in production, but not enough to cause the large drop in loading. Two changes inside the tannery probably account for the major drop.

Much less water is now being used in the cowhide fleshing operation, and the great bulk of the fleshings are now collected from the floor and hauled to landfill rather than being flushed down the drain to the treatment plant. In addition, a screen has been installed inside the building to trap large solids before they leave the plant. This action probably did not have as much effect as the first one mentioned, however, because the treatment plant was preceded by a slotted screen anyway.

Chrome tanning liquor and vegetable tanning liquor are now being hauled directly to the landfill rather than discharged to the treatment plant. The chromium is precipitated by lime in the tank truck before discharge.

Whether or not the reasons outlined above completely or adequately account for the decrease in waste load to the plant is problematical, but is the best explanation which plant personnel can advance. A definite answer could be obtained only by another complete waste survey.

Operation of the treatment plant itself has also improved. Operator experience and competence has increased. Most pumps have been replaced and the new ones run much more smoothly and reliably, eliminating most of the clogging problems, and the surges associated with the previous off-on operation. The secondary clarifier efficiency is the primary beneficiary of this program. This was the major problem identified during the EPA survey.

It cannot be stated with certainty, but it is probable that the waste treatment plant could now accept a much greater organic load, approaching the design load, without a great decrease in performance efficiency. These results again demonstrate that satisfactory waste treatment for an alum tannery is possible, if due care is taken in process and plant design, and if competent and conscientious operation is provided.

ACKNOWLEDGEMENTS

The material in this report is based on a variety of sources, but three deserve special mention. The section on the original laboratory studies is based on a report by H. D. Tomlinson, E. L. Thackston, V. W. McCoy, and P. A. Krenkel. The design material is based on the preliminary design report by J. Wiley Finney of Howard K. Bell, Consulting Engineers, Inc. The material on the EPA survey comes largely from a preliminary report by Ed Berg, who was in charge of the EPA industrial waste survey team. The contributions of all are gratefully acknowledged.

The author would also like to acknowledge the outstanding cooperation and patience, over the entire five years of this project, of the officials of the Caldwell Lace Leather Co., particularly J. Richard Howlett, President, and Jim Moore, Vice-President.

This project was supported by the U. S. Environmental Protection Agency, and its agency predecessors, through research and demonstration grant No. WPRD 25-01. The support, encouragement, advice, and patience of the project officers, James Kreissl and James Westrick, is gratefully acknowledged.

The aid of Mrs. Betty Faris in the preparation of the manuscript of the final report is also gratefully acknowledged.

Preceding page blank

REFERENCES

1. Tomlinson, H. D., E. L. Thackston, P. A. Krenkel, and V. W. McCoy, "Complete Treatment of Tannery Wastes," Tech. Report No. 15, Sanitary and Water Resources Engineering, Vanderbilt University, Nashville, Tennessee, 1968.

2. Tomlinson, H. D., E. L. Thackston, P. A. Krenkel, and V. W. McCoy, "Laboratory Studies of Tannery Waste Treatment," Journal, Water Pollution Control Federation, 41, 4, 660, April, 1969.

3. Spiers, C. H., "The Wastes of the Leather Industry," National Leathersellers College, London, England, SEI.

4. Sutherland, R., "Industrial Wastes--Tanning Industry," Ind. and Eng. Chem., 39, 628, 1947.

5. Harnly, J. W., "Liquid Industrial Wastes--Tanneries," Ind. and Eng. Chem., 44, 520, 1952.

6. Industrial Waste Guide, Supplement D, Ohio River Pollution Survey, U. S. Public Health Service, Washington, D. C., 1944.

7. Masselli, J. W., N. W. Masselli, and M. G. Burford, "Tannery Wastes--Pollution Sources and Methods of Treatment," New England Interstate Water Pollution Control Commission, Boston, Mass., 1958.

8. O'Flaherty, F., "Leather." Rept. and Papers of the Res. Lab. of the Tanners' Council of America, Inc., IX, 485, 1965

9. Eye, J. D., "The Treatment and Disposal of Tannery Wastes," Rept. and Papers of the Res. Lab. of the Tanners' Council of America, Inc., IX, 438, 1965.

10. Southgate, B. A., "Symposium on Liquid Industrial Wastes--Waste Disposal in Britain," Ind. and Eng. Chem., 44, 524, 1952.

11. Villa, L., "Waste-Water in the Tanning Industry and its Purification," Jour. Amer. Leather Chemists Assn., 61, 414, 1966.

Preceding page blank

12. Haseltine, T. R., "Tannery Wastes Treatment with Sewage at Williamsport, Pennsylvania," Sewage and Industrial Wastes, 30, 1, 65, Jan 1958.

13. Warrick, L. F., and E. J. Beatty, "Treatment of Tannery Wastes with Domestic Sewage," Sew. Works Jour., 8, 122, 1936.

14. Porter, W., "Operating Problems from Tannery Wastes at Ballstan Spa., N. Y.," Sew. Works Jour., 21, 7, 738, July, 1949.

15. Power, R. M., "The Treatment of Tannery Wastes With Sanitary Sewage at Ayer," Sanitalk, 5, 4, 19, 1957.

16. Rosenthal, B. L., "Treatment of Tannery Waste--Sewage Mixture on Trickling Filters," Sanitalk, 5, 4, 21, 1957.

17. Rosenthal, B. L., "Treatment of Tannery Wastes by Activated Sludge," Sanitalk, 6, 1, 7, 1957.

18. Taylor, W. H., "Disposal of Tannery Wastes," Sanitalk, 1, 4, 24, 1953.

19. Nemerow, N. L., and R. S. Armstrong, "Proto-type Studies of Combined Treatment of Wastes from 22 Tanneries and Two Municipalities," Proc. 22nd Ind. Waste Conf., Purdue Univ., Lafayette, Indiana, 1967.

20. Nemerow, N. L., and R. S. Armstrong, "Combined Tannery and Municipal Waste Treatment, Gloversville--Johnstown, N. Y.," Proc. 21st Ind. Waste Conf., Purdue Univ., Ext. Ser. 121, 447, 1966.

21. Wims, F. J., "Treatment of Chrome Tanning Wastes for Acceptance by an Activated Sludge Plant," Proc. 18th Ind. Waste Conf., Purdue Univ. Ext. Ser. 115, 534, 1963.

22. Filbert, J. W., and R. E. Pailthorp, "Biological Waste Treatment in the Chrome Tannery," Leather and Shoes, 14, Dec, 1967.

23. Parker, R. R., "Disposal of Tannery Wastes," Proc. 22nd Ind. Waste Conf., Purdue Univ., Lafayette, Indiana, 1967.

24. Berg, N., T. H. Miller, A. P. Pearce, S. G. Shuttleworth, and D. A. Williams-Wynn, "Studies on Elimination of Sulfide from Tannery Beamhouse Effluents by Manganese Catalyzed Oxidation," Jour. Amer. Leather Chemists Assn., 62, 684, 1967.

25. Sproul, O. J., P. F. Atkins, and F. E. Woodard, "Investigations on Physical and Chemical Treatment Methods for Cattle Skin Tannery Wastes," Journal WPCF, 38, 4, 508, April, 1966.

26. Sproul, O. J., K. Keshavan, and R. E. Hunter, "Extreme Removals of Suspended Solids and BOD in Tannery Wastes by Coagulation with Chrome Tan Dump Liquors," Proc. 21st Ind. Waste Conf., Purdue Univ. Ext. Ser. 121, 600, 1966.

27. Eye, J. D., and S. P. Graef, "Literature Survey on Tannery Effluents," Jour. Amer. Leather Chemists Assn., 62, 194, 1967.

28. Rich, L. G., Unit Operations of Sanitary Engineering, John Wiley and Sons, New York, N. Y., 1961.

29. Eye, J. D., and S. P. Graef, "Pilot Plant Studies on the Treatment of Tannery Wastes," unpublished manuscript.

30. Woodard, F. E., and J. E. Etzel, "Coacervation and Chemical Coagulation of Lignin from Pulp Mill Black Liquor," Journal WPCF, 37, 7, 990, July, 1965.

U. S. GOVERNMENT PRINTING OFFICE: 1973—514-155/294